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HIGH-STRENGTH, BROADBAND, LIGHTWEIGHT SILICON OXIDE RADOME TECHNIQUES

J. N. Harris, S. H. Bomar, Jr., and E. A. Welsh
Engineering Experiment Station, Georgia Institute of Technology

TECHNICAL REPORT AFAL-TR-68-71

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HIGH-STRENGTH, BROADBAND, LIGHTWEIGHT
SILICON OXIDE RADOME TECHNIQUES

J. N. Harris, S. H. Bomar, Jr., and E. A. Welsh

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ABSTRACT

Development of low and high-density, high-strength, amorphous silica for the construction of A-sandwich radomes is discussed. Techniques are described for forming low-density, high-strength structures by filament winding, slip-casting of honeycomb structures, and foaming of ultra-high purity amorphous silica. High-density structures were slip-cast from a high purity slip formed by consolidation and subsequent ball milling of Cab-O-Sil[®], a synthetic amorphous silica "fluff." The elastic modulus of the low-density material was increased to 1.5 times that available from commercial fused silicas. Densities of 98 per cent of theoretical and elastic moduli of 9×10^6 psi, approximately twice that attainable with commercial slip-cast fused silica, were achieved with the high-density material. Firing times of 60 hours at 2200° F were possible without excessive cristobalite formation in the high purity silica as compared with 3 to 4 hours which was the maximum sintering time for commercial fused silicas without excessive devitrification.

FOREWORD

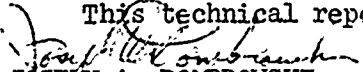
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This report covers the period of work from 1 March 1967 to 29 February 1968 and is the first of three annual Summary Reports to be published under this contract. (Georgia Tech Project A-1004).

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This report was submitted by the authors 1 March 1968.

This technical report has been reviewed and is approved.


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SECTION I

INTRODUCTION

The outstanding thermal properties of fused silica should allow the achievement of the following thermal design goals.

- (1) A 10 GHz half wave wall radome that will withstand a sudden thermal shock from ambient to 4000° F to the external surface.
- (2) Continuous operation of the radome structure (with no thermal cycling) at an outside surface temperature of 2000° F, indefinitely.
- (3) Satisfactory operation of the radome for 1000 hours with thermal cycling up to 1800° F.
- (4) Satisfactory operation of the radome for at least 30 seconds with surface temperatures up to 6000° F.

Also, the superior electrical properties of fused silica should allow the following electrical limitations to be placed on the radome structure.

- (1) The total effective dielectric constant of the radome structure shall not exceed 2.2.
- (2) The loss tangent shall not be greater than 0.001, at room temperature and 9.375 GHz.

Other significant design goals for a lightweight, broadband, fused silica radome, which are dependent on the specific construction details, are:

- (1) The weight shall not exceed two-thirds that of a monolithic structure of the same size and design center frequency.
- (2) The bandwidth at normal incidence shall be at least $\pm 20\%$ of the design frequency with minimum transmission efficiencies of 85% for linear parallel polarization, at angles of incidence up to $\pm 45^\circ$.
- (3) The reflection coefficient shall be less than 2% of the impinging energy throughout the temperature range.
- (4) The boresight error shall not be greater than 2 milliradians at angles of incidence $\pm 45^\circ$.

During the past year the design fabrication and physical properties of fused silica "A" sandwich radomes were investigated under U. S. Air Force Contract AF 33(615)-3445. However, this research indicated that the conventional fabrication techniques for the foamed and the slip-cast fused silica are inadequate for the attainment of one of the major design goals, lightweight. That is, it is presently not possible to fabricate slip-cast fused silica skins of the necessary thinness, or foamed fused silica cores of low enough density to meet the design goal of two-thirds of the weight of a monolithic structure having the same size and design center frequency.

Should the necessary fabrication techniques be developed, with the presently available mechanical properties of slip-cast or foamed fused silica the load bearing capabilities of an "A" sandwich radome of practical size would be significantly inferior to that of a monolithic radome of equal size^{*}. There-

^{*}Should the requirement be for an electromagnetic window (segment as opposed to total radome) the load bearing capability would be significantly superior to a monolithic window of the same size.

fore, it is necessary to develop unique fabrication methods and techniques for improving mechanical properties so that the outstanding thermal and electrical properties of fused silica can be utilized in an "A" sandwich radome. The results of the investigations under AF 33(615)-3445 have indicated that these methods and techniques must provide skins having mechanical properties on the order of twice those presently available with SCFS, and cores having mechanical properties about four times those presently available from fused silica foam.

Advancements in fused silica technology accomplished during the past year under U. S. Air Force contracts AF 33(615)-3445, AF 33(615)-3330, U. S. Navy contract NO# 63-0143-d, and Georgia Tech-funded in-house research programs have shown that the following approaches are promising for providing the necessary methods and fabrication techniques.

- (1) Optimization of the particle size distribution, and/or control of impurities in the fused silica.
- (2) Inclusion of high strength filamentary reinforcements in the SCFS accompanied by vibration during slip-casting and/or high-temperature vacuum sintering.
- (3) Filament winding.

SECTION II

EXPERIMENTAL PROGRAM

1. - Development of Low-Density, High-Strength Structures

a. Filament Winding

Studies were initiated to examine the feasibility of low-density, high-strength, filament-wound cores for "A" sandwich radome construction. The filament wound core should be an all amorphous silica system to obtain the desired thermal and dielectric properties.

Initial studies were made utilizing 20-end fused quartz roving and the all amorphous silica binder developed under contract AF 33(615)-3330 1/. The composition of this binder is:

58 w/o Polysilicic acid solution*

40 w/o Spray dried -325 mesh fused silica

2 w/o Cab-O-Sil[®] (colloidal silica)

Experiments were initiated to determine whether advantage could be taken of variations in winding patterns to produce significantly lower densities than were obtained under contract AF 33(615)-3330 using the same filament/binder system. Helical winding patterns were varied by changing the winding angle and the number of circuits per pattern. (See Appendix for filament winding terminology definitions.)

All specimens were right circular cylinders approximately 12 inches in length and were wound on a 3-inch diameter mandrel. The filament winding machine was set-up to produce the configurations shown in Table I. After

*Prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) with 0.05 N hydrochloric acid in a ratio of 20.8 ml of HCl solution to 100 ml of TEOS.

TABLE I
FILAMENT WINDING CONFIGURATIONS OF FUSED SILICA COMPOSITE
SPECIMENS FOR DENSITY AND TENSILE
STRENGTH DETERMINATIONS

<u>Winding Angle</u> (degree)	<u>No. of Circuits Per Pattern</u>
32-1/2	5
32-1/2	10
45	5
45	11
57-1/2	5
57-1/2	9

winding, all specimens were dried at 120° F for 16 hours and cured at 600° F for 4 hours. The specimens were then removed from the mandrel and cut into 1/2-inch wide rings. Several rings from each cylinder were sintered at 1000°, 1500°, and 1800° F for 4 hours.

Porosity, bulk density, and theoretical density were determined for each specimen using a method similar to ASTM C 373-56, "Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Porous Whiteware Products." The values obtained in this test are shown in Table II.

Tensile strength was determined using a modified version of ASTM D-2290-64T "Apparent Tensile Strength of Parallel Reinforced Plastics by Split Disk Method." That is, two half-circles were placed inside the rings and pins passed through holes at the center of gravity of each ring. The pins were in turn held by forks fastened in a universal testing machine. The assembled

TABLE II

APPARENT POROSITY AND BULK DENSITY FOR FILAMENT WOUND
FUSED SILICA COMPOSITES SINTERED AT 600° F,
1000° F, 1500° F, AND 1800° F

<u>Winding Angle</u> (degree)	<u>Number of Circuits Per Pattern</u>	<u>Heat Treatment Temperature</u> (°F)	<u>Apparent Porosity</u> (v/o)	<u>Bulk Density</u> (lb/ft ³)
32-1/2	5	600	44	75
		1000	47	73
		1500	47	73
		1800	48	71
32-1/2	10	600	49	68
		1000	44	76
		1500	44	74
		1800	45	74
45	5	600	40	82
		1000	45	75
		1500	47	72
		1800	45	76
45	11	600	51	71
		1000	45	75
		1500	47	72
		1800	45	76
57-1/2	5	600	39	82
		1000	40	81
		1500	40	82
		1800	40	82
57-1/2	9	600	40	80
		1000	42	80
		1500	42	81
		1800	42	82

rig is shown in Figure 1. A load was applied to stress the rings in tension to ultimate failure. Tensile strength was calculated from the applied load divided by the cross-sectional area under stress. Tensile strength values are given in Table III.

TABLE III

TENSILE STRENGTH OF FUSED SILICA COMPOSITES SINTERED AT
600° F, 1000° F, 1500° F, AND 1800° F

Specimen	Circuits/Pattern	Tensile Strength (psi)			
		Sintering Temperature			
Winding Angle (degrees)		600° F	1000° F	1500° F	1800° F
32-1/2	5	294	370	393	625
32-1/2	10	869	275	495	399
45	5	1949	1620	1219	1052
45	11	1486	822	572	617
57-1/2	5	2512	1745	1556	1370
57-1/2	9	1855	1863	1319	1250

The filament winding studies did not result in a system with enough flexibility to allow lowering of the composite density to a point where the composite could be used as a core in a fused silica "A" sandwich radome. No composites were obtained with densities less than 70 lb/ft³ and these composites had low tensile strengths. Two possible methods for obtaining a lower density and improving the tensile strength would be: (1) Modification of the binder, and (2) A change in the type of reinforcement. Therefore, a program was initiated to study the properties of all inorganic composites utilizing a woven fused

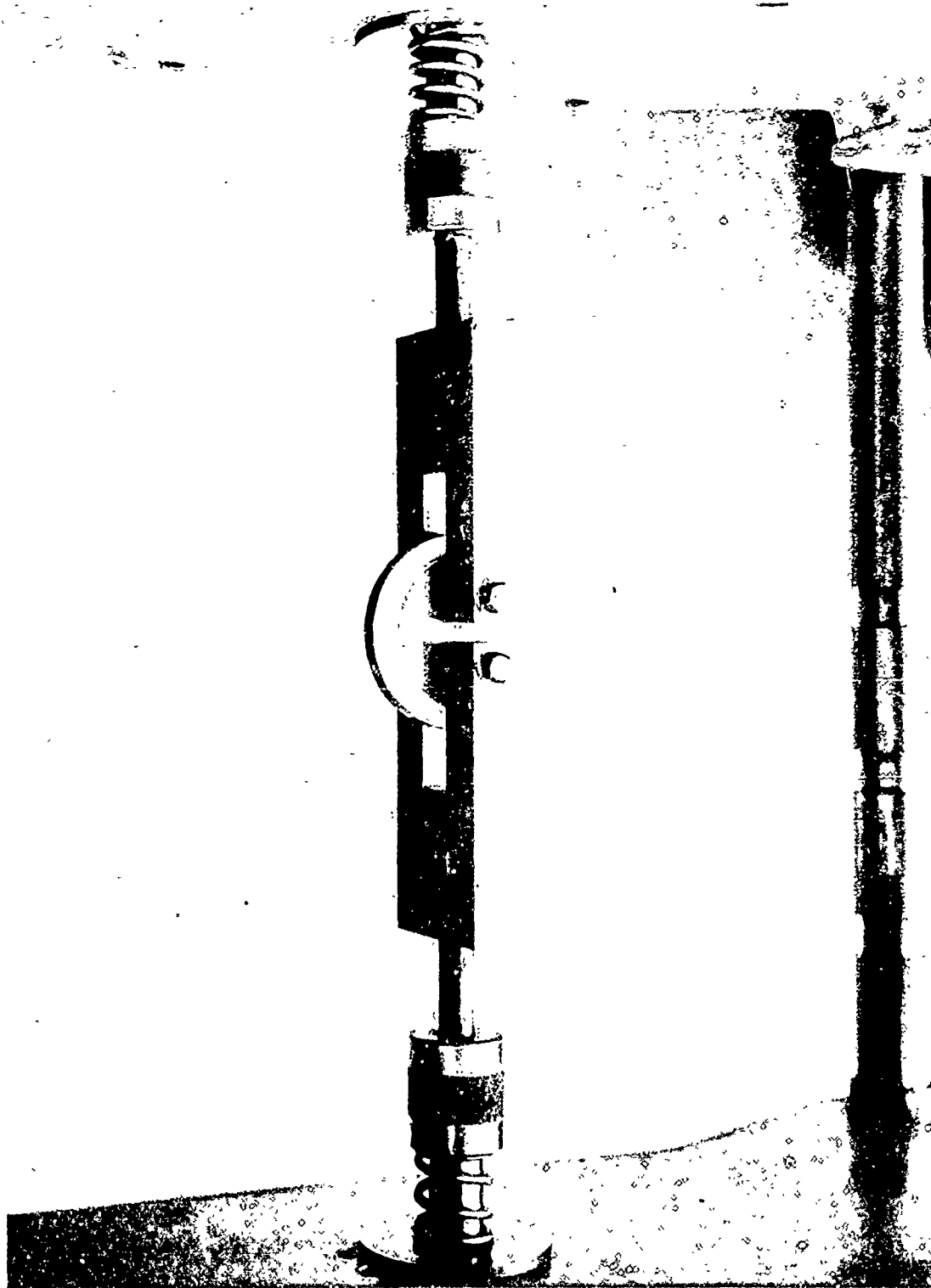


Figure 1. "D" Plates, Hangers and Filament Wound Fused Silica Ring Assembled and Mounted in Universal Testing Machine.

silica cloth to provide bi-directional reinforcement, and both fused silica slip and the 58-40-2 binder developed under U. S. Air Force Contract AF 33(615)-3330 1/ as the matrix material.

Some of the major problems with the inorganic binders have been obtaining proper wetting of the reinforcing material by the binder and obtaining a sufficient volume percentage of matrix in the final composite. Another problem is that the final sintered matrix obtained when using either fused silica slip or the 58-40-2 binder is too dense to produce a composite core for "A" sandwich construction. One possible method which should aid in increasing the volume percentage of matrix in the final composite and at the same time produce a more porous matrix would be the incorporation of an organic carrier material along with the fused silica cloth and the binder in the composite. The organic carrier material selected for this purpose was cotton gauze in tape form. In forming a composite alternate layers of cotton gauze and fused silica cloth were saturated with the inorganic binder and laid up to form the final structure.

Initial experiments were conducted using the cotton gauze and binders only to determine how much the matrix material could be reduced in density and the effect on properties such as modulus of rupture and rate of devitrification.

The two potential binders examined were fused silica slip and the 58-40-2 binder used in previous filament winding studies. Strips of cotton gauze were saturated with the binder and then laid up into rectangular bars approximately 1/4-inch thick. The lay ups were made on aluminum screen and each layer was thoroughly squeegeed to remove any entrapped air. All specimens were dried overnight at room temperature, and then at 200° F for 24 hours. The volume

per cent gauze and volume per cent matrix were calculated to be approximately 12 and 88 per cent respectively using fused silica slip and 27 and 73 per cent respectively using the 58-40-2 binder. The specimens were then dried at 400° F for one hour and at 600° F for two hours. The furnace used as a dryer was then raised in temperature to 1000° F. Upon reaching 1000° F all specimens were quickly transferred to another furnace at 1000° F for subsequent heat treating. The firing schedule for the 1800° F firings is shown in Figure 2 and the firing schedule for the 2200° F firings in Figure 3. In each case specimens were held at maximum temperature for two hours.

Porosity, bulk density, and theoretical density of all specimens were calculated from data obtained by air displacement. These values are shown in Table IV. Modulus of rupture data using three point-center point loading on a 2-inch span (span to depth ratio > 8:1) are shown in Table V.

TABLE IV
POROSITY, BULK DENSITY, AND THEORETICAL DENSITY OF STRUCTURES
PREPARED FROM COTTON GAUZE AND SILICA BINDERS

<u>Binder</u>	<u>Sintering Temperature</u> (°F)	<u>Porosity</u> (v/o)	<u>Bulk Density</u> (gm/cc)	<u>Theoretical Density</u> (gm/cc)
Fused Silica Slip	1800	27.2	1.40	1.92
		34.4	1.37	2.10
	2200	34.5	1.36	2.09
			1.42	2.24
58-40-2*	2200	55.0	1.03	2.29
		50.0	1.06	2.11

*Samples fired at 1800 F were too fragile to measure.

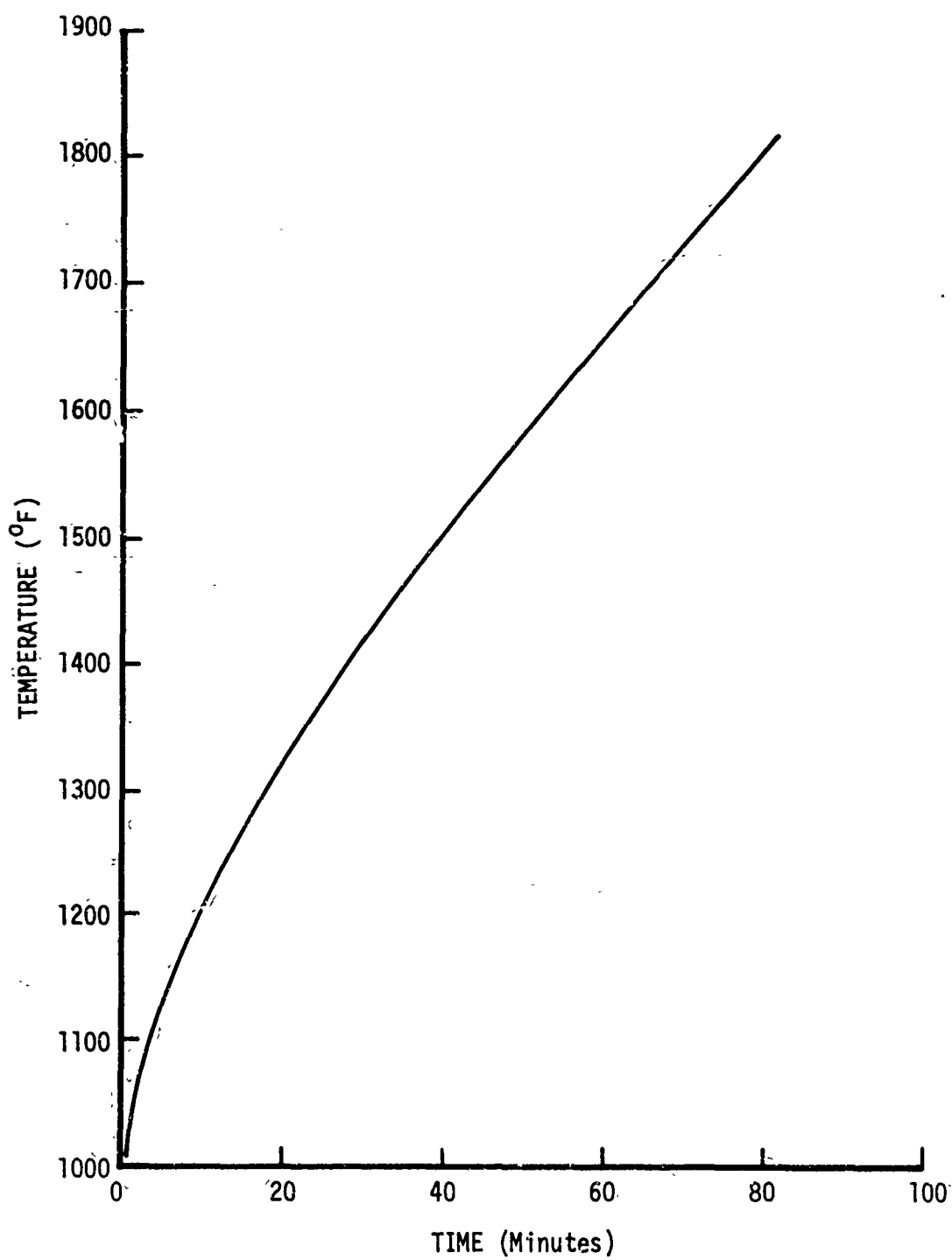


Figure 2. Rate of Temperature Increase for Cotton Gauze-Silica Binder Composites Sintered at 1800° F.

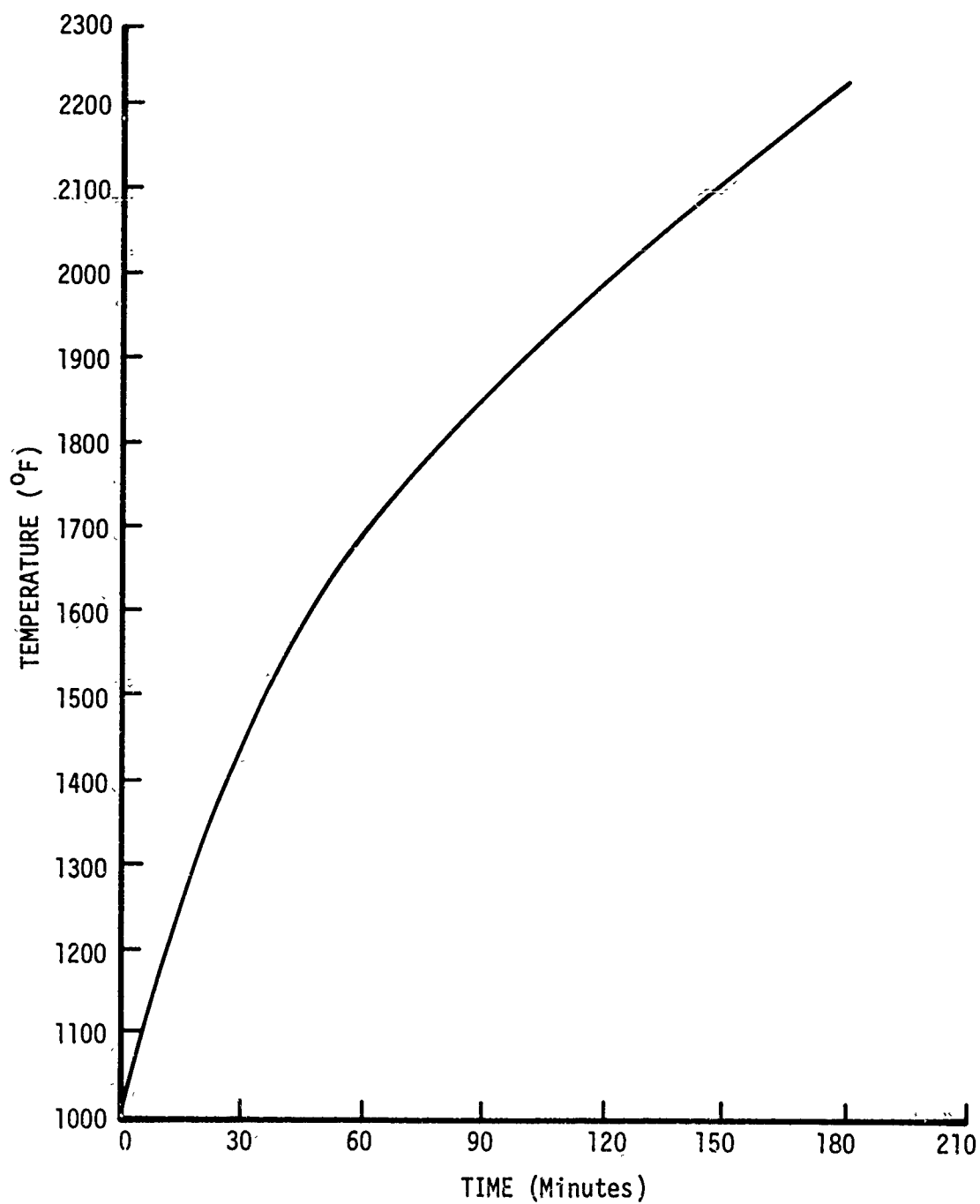


Figure 3. Rate of Temperature Increase for Cotton Gauze-Silica Binder Composites Sintered at 2200° F.

TABLE V
MODULUS OF RUPTURE OF STRUCTURES
PREPARED FROM COTTON GAUZE AND SILICA BINDERS

<u>Binder</u>	<u>Sintering Temperature</u> (°F)	<u>Modulus of Rupture</u> (lb/in ²)
Fused Silica Slip	1800	270
		207
	2200	139
		213
58-40-2*	2200	47
		51

* No measurements made at 1800° F.

The decrease in modulus of rupture and the appearance of the bars made with both fused silica and the 58-40-2 binder indicated the presence of a large volume per cent of devitrified material. To determine whether the impurities on or in the cotton gauze were responsible for the rapid rate of devitrification or if it was caused by a combination of impurities in the binders and gauze, samples were prepared only with the highest purity binder components (i.e. the Cab-O-Sil[®] and polysilicic acid). These specimens were dried and fired at 2200° F for 3-1/3 hours. The cristobalite content was found to average 37.5 v/o. This indicated that the cotton gauze was responsible for the high devitrification rate since these high purity binder materials exhibit cristobalite contents on the order of 0.0 to 0.6 v/o when fired to the 2200° F temperature without the gauze.

The mineralizers transported by the cotton gauze were thought to be on the surface in the form of a size or finish applied to aid in weaving or

retaining the sterile quality of the gauze, or the mineralizers might be inherent in the cotton used to weave the gauze. The exact source of contamination was determined through spectrographic analyses of "as received" cotton gauze, boiled and washed cotton gauze, and the distilled water used in boiling the gauze. The analysis of the cotton gauze indicated the presence of small amounts of magnesium, iron, copper, silver, and calcium. Whereas, the cotton boiled in deionized water for one hour and then thoroughly rinsed twice with deionized water revealed essentially no iron or silver and much smaller quantities of magnesium, copper, and calcium.

The following study was then undertaken to decrease the rate of devitrification of fused silica-cotton gauze lay-ups. A silica body was formed from a 95 w/o polysilicic acid solution and 5 w/o Cab-O-Sil[®] by allowing liquid to evaporate from this viscous liquid slurry. After careful and thorough drying, first at room temperature then overnight at 450° F, the body was fired at 2200° F for 3-1/3 hours. Using the same silica binder composition, lay-ups were made with as-received and with washed cotton gauze. These lay-ups were dried overnight at 125° F, at 600° F for one hour, and 1000° F for two hours. They were then fired 3-1/3 hours at 2200° F. The volume per cent cristobalite in the three sets of bars is presented in Table VI. As can be seen with the water washed cotton gauze, there is a significant reduction in devitrification as compared to the as-received cotton gauze.

Since the washed cotton gauze seemed to contribute very little to the composite devitrification rate, some of the above work was repeated. That is, composites were laid up with washed cotton gauze and Glasrock[®] fused silica slip or with a binder consisting of 58 w/o polysilicic acid, 40 w/o dried and reground Glasrock[®] slip and 2 w/o Cab-O-Sil[®] M-5 colloidal silica. The bars

TABLE VI

EFFECT OF IMPURITIES ON THE DEVITRIFICATION OF STRUCTURES PREPARED
FROM COTTON GAUZE AND A SILICA BINDER AND SINTERED
AT 2200° F FOR TWO HUNDRED MINUTES

<u>Composition of Structure</u>	<u>Average Cristobalite Content</u> (v/o)
Binder Only (95 w/o Polysilicic Acid) (5 w/o Cab-O-Sil®)	0.1
Binder and Washed Cotton Gauze	0.5
Binder and As-Received Gauze	27.2

were dried overnight at 125° F, then placed in a furnace at 200° F. The furnace temperature was increased to 1000° F at a rate of rise of 200° F per hour. The furnace was held at 1000° F for 1 hour to insure complete oxidation of the cotton gauze. The bars were then transferred to a 2200° F furnace and sintered at temperature for 3-1/3 hours. The bars were removed from the furnace, cooled and elastic modulus and cristobalite content measured. The bars were then returned to the 2200° F furnace and sintered for an additional hour. After removing the bars from the furnace and allowing them to cool, cristobalite content and elastic modulus were again measured. The bars were then broken transversely using three point center point loading and modulus of rupture calculated. Table VII presents the data for elastic modulus, cristobalite content, bulk density, and modulus of rupture for the specimens prepared with the washed cotton gauze. A comparison of the data in Table VII with the data in Tables IV and V shows a ten fold increase in modulus of

TABLE VII

PROPERTIES OF STRUCTURES PREPARED FROM WASHED COTTON
GAUZE AND SILICA BINDERS

<u>Binder</u>	<u>Sintering Time at 2200° F</u> (min)	<u>Cristobalite Content</u> (v/o)	<u>Bulk Density</u> (gr/cc)	<u>Elastic Modulus</u> (10 ⁶ psi)	<u>Modulus of Rupture</u> (psi)
58-40-2	200	1.5	0.72	0.0713	---
	200	2.4	0.80	0.0767	---
	260	3.1	0.72	0.0861	60
	260	3.6	0.81	0.0867	77
Slip	200	9.6	1.36	1.92	---
	200	8.9	1.26	1.78	---
	260	12.6	1.37	1.97	1721
	260	12.9	1.26	1.79	2333

rupture for specimens having a slip-cast fused silica binder and only a slight increase for those made with the 58-40-2 binder. It should be noted that the smaller increase in strength with the 58-40-2 binder is partially due to the lower density of the specimens made with the washed cotton gauze. This lower density was a result of failure to remove all the air during fabrication rather than to any differences in fabrication technique.

One possible method of producing a porous, all fused silica composite with fused silica fiber reinforcement would be by filament winding using alternate layers of an open weave organic fiber (cotton gauze) cloth and a fused silica reinforcement. Saturation of the cotton gauze with the binder material would increase the volume per cent binder in the final sintered

structure. It would also give a porous structure due to burn out of the cotton on firing. Structures of lower density could be produced by using two or more layers of cotton gauze to every layer of fused silica reinforcement.

The use of woven fused silica cloth as the reinforcement would be preferred as it would give reinforcement in two directions and the binder would fill the openings in the cloth. This should provide a better mechanical lock between binder and fiber and prevent the shear that is common in filament wound systems prepared with a continuous roving. However, fused quartz yarns cannot be satisfactorily woven into a cloth without a protective size or finish on the yarn. The fused quartz cloths available commercially are finished with materials which are alkaline in nature and cause rapid devitrification of the cloth above 2000° F. Complete removal of these finishes is difficult and unless they are immediately replaced with another finish the cloth is severely weakened from abrasion of the yarns against themselves. Of course, any trace of impurities left on the yarn will result in rapid devitrification of the composite.

The high cost of commercial fused silica cloth and the attendant devitrification problems as a result of the available finishes makes the approach of using the presently available commercial fused silica cloths in a high purity fused silica composite unattractive at this time. However, in order to continue the investigation using an organic carrier material which would burn out on firing and hence provide a porous composite, it was decided to incorporate fused silica roving into the composite rather than the fused silica cloth.

The fused silica roving provides strength reinforcement in one direction only as opposed to the two directional reinforcement expected from a woven cloth. However, use of the roving should provide a composite structure with a density similar to that which would be expected with alternate layers of cotton and fused silica cloths. It should also indicate if reinforcement is obtained from fused silica fibers when sintered in an all fused silica composite at 2200° F.

A fused silica roving without any size or finish was obtained from the J. P. Stevens Company. This material was examined for rate of devitrification in a composite system by dipping small segments of the roving (bows) in a suspension of 5 w/o Cab-O-Sil[®] M-5 colloidal silica, in polysilicic acid. After drying the bows were fired for 3-1/3 hours at 2200° F, cooled, and examined for bulk cristobalite by x-ray diffraction. On the average less than 6.5 v/o cristobalite was found in the specimens.

This particular roving could be used for filament winding only with the greatest care and obviously could not be used for weaving of cloth. The lack of a finish or size on the roving causes it to abrade against itself and to break under low tensile stress. The normal procedure for protecting a roving is to apply a surface treatment which reduces this self abrasion. Many of these protective finishes are organic and their protection diminishes with increasing temperature. Under Contract AF 33(615)-3330 1/ it was shown that the tensile strength of fused silica roving protected with a starch oil size had a tensile strength too low to measure above 1200° F. The same roving protected with an aluminum oxide film provided from an aluminum chelate coating had a tensile strength of 39,000 psi at the same temperature.

Unfortunately the aluminum chelate coating and other surface treatments which have worked well on fused silica rovings at low temperature have caused difficulty above 2000° F by appearing to promote devitrification. This has been attributed mostly to alkali elements present in the surface coatings. However, in the work under Contract AF 33(615)-3330 filament wound composites prepared with aluminum chelate treated fused silica rovings devitrified at a more rapid rate than those made with a fused silica roving having an organic starch-oil size.

Work under the same contract indicated that the rate of devitrification of fused silica was influenced by the level of impurities in the fused silica. It appeared that a threshold level of impurities existed beyond which the rate of cristobalite growth changed at a rapid rate. However, this level was not determined, nor were the specific impurities responsible for devitrification determined.

Since the J. P. Stevens roving exhibited a low rate of devitrification it was felt worthwhile to determine whether a very thin layer of aluminum oxide on the surface of the roving (provided from the aluminum chelate coating) would increase the rate of devitrification.

Samples of the unsized J. P. Stevens roving were coated by dipping into a solution composed of 8 w/o 8-hydroxy quinoline and 92 w/o toluene. The samples were thoroughly saturated and then transferred to a solution containing 10.4 w/o aluminum isopropoxide and 89.6 w/o toluene. These samples were dried overnight and cured at 600° F for 30 minutes. Six of these samples, along with six untreated samples of the J. P. Stevens roving, were placed in a furnace at 2200° F. After each 4 hours one treated and one untreated sample were removed from the furnace and cristobalite determined by x-ray diffraction. The results of this study are shown in Table VIII.

TABLE VIII
EFFECT OF ALUMINUM CHELATE FINISH ON THE RATE OF CRISTOBALITE
GROWTH AT 2200° F IN FUSED SILICA ROVING

Firing Time (hr)	Volume Per Cent Cristobalite	
	Untreated	Treated
4	0.40 ± 0.30	1.09 ± 0.80
8	0.24 ± 0.04	0.42 ± 0.10
12	0.85 ± 0.04	0.73 ± 0.14
16	0.35 ± 0.07	7.79 ± 0.36
20	0.69 ± 0.14	17.90 ± 0.67
24	0.96 ± 0.17	24.53 ± 0.27

Composite bars were prepared with alternate layers of washed cotton gauze and the fused silica roving by filament winding on a flat mandrel. One-inch wide gauze was used and it was saturated with fused silica slip as it was wound onto the mandrel. After a 1/2-inch thick composite was built up from alternate layers of cotton gauze and fused silica roving, the composite was dried on the mandrel at room temperature overnight. It was then removed from the mandrel and placed in a furnace at 200° F. The temperature of the furnace was increased at a rate of rise of 200° F per hour until 1000° F was reached. The furnace was then held at 1000° F for 4 hours to oxidize all of the organic material. The composite was then transferred to a furnace at 2200° F and sintered for 2 hours and 45 minutes.

The elastic modulus, bulk density, cristobalite content, and modulus of rupture were measured on 5 bars cut from this composite. These values are shown in Table IX.

TABLE IX

PROPERTIES OF COTTON GAUZE FUSED SILICA ROVING-
FUSED SILICA BINDER COMPOSITES

<u>Sintering Time at 2200° F</u>	<u>Cristobalite Content</u>	<u>Bulk Density</u>	<u>Elastic Modulus</u>	<u>Modulus of Rupture</u>
(min)	(v/o)	(gm/cc)	(10 ⁶ psi)	(psi)
165	8.3	1.49	2.79	2164

b. Foamed High Purity Fused Silica Slips

A high purity fused silica slip was produced by wet milling broken pieces of General Electric 204 fused silica glass in high alumina ball mills. Prior to milling, the G. E. 204 glass was cleaned in dilute hydrochloric acid to remove surface impurities. A foam was prepared from this slip using the following procedure.

(1) Foam Formulation:

1000 cc of fused silica slip

35 cc of 1.5 N hydrochloric acid

12.5 cc water

12.5 cc non-ionic detergent

(2) Foaming Procedure:

The water and acid were added with slow mixing.

The detergent was added and high speed agitation provided with an electric mixer. The resultant

foam was dried in a paper mold and fired for 6 hours

at 2200° F. The resultant foam had an approximate density of 25 lb/ft³.

To determine optimum strength, specimens were fired at 2200° F at additional intervals of 2 hours. After each interval measurements were made for elastic modulus, bulk density, and cristobalite content. Over the 41 hour firing cycle bulk density of the foam increased from 23 to 27.5 pounds per cubic foot. Plots of cristobalite content versus firing time and elastic modulus versus firing time are shown in Figure 4 and bulk density versus time in Figure 5. An insufficient quantity of the foam was available to determine modulus of rupture.

A second foam sample was prepared from Aeroceram 50[®] slip^{*}. This is a commercial fused silica slip which is reportedly of a higher purity than that normally commercially available. Laboratory investigations of dense slip-cast fused silica bars made from this slip have indicated that the physical and mechanical properties are very similar to those of bars made from G. E. 204 slip. Therefore, this slip was used to continue the foam study in lieu of the G. E. 204 slip which was in short supply.

The same foaming procedure as described for the nominally 25 lb/ft³ foam was used except beating time was shorter, thereby producing a foam of nominally 45 lb/ft³ density. This foam was fired initially for 10 hours then in 4 hour increments for a total of 78 hours. Plots of cristobalite content versus firing time and elastic modulus versus firing time are shown in Figure 6 and bulk density versus firing time in Figure 7.

* Aeroceram Incorporated
Gardena, California.

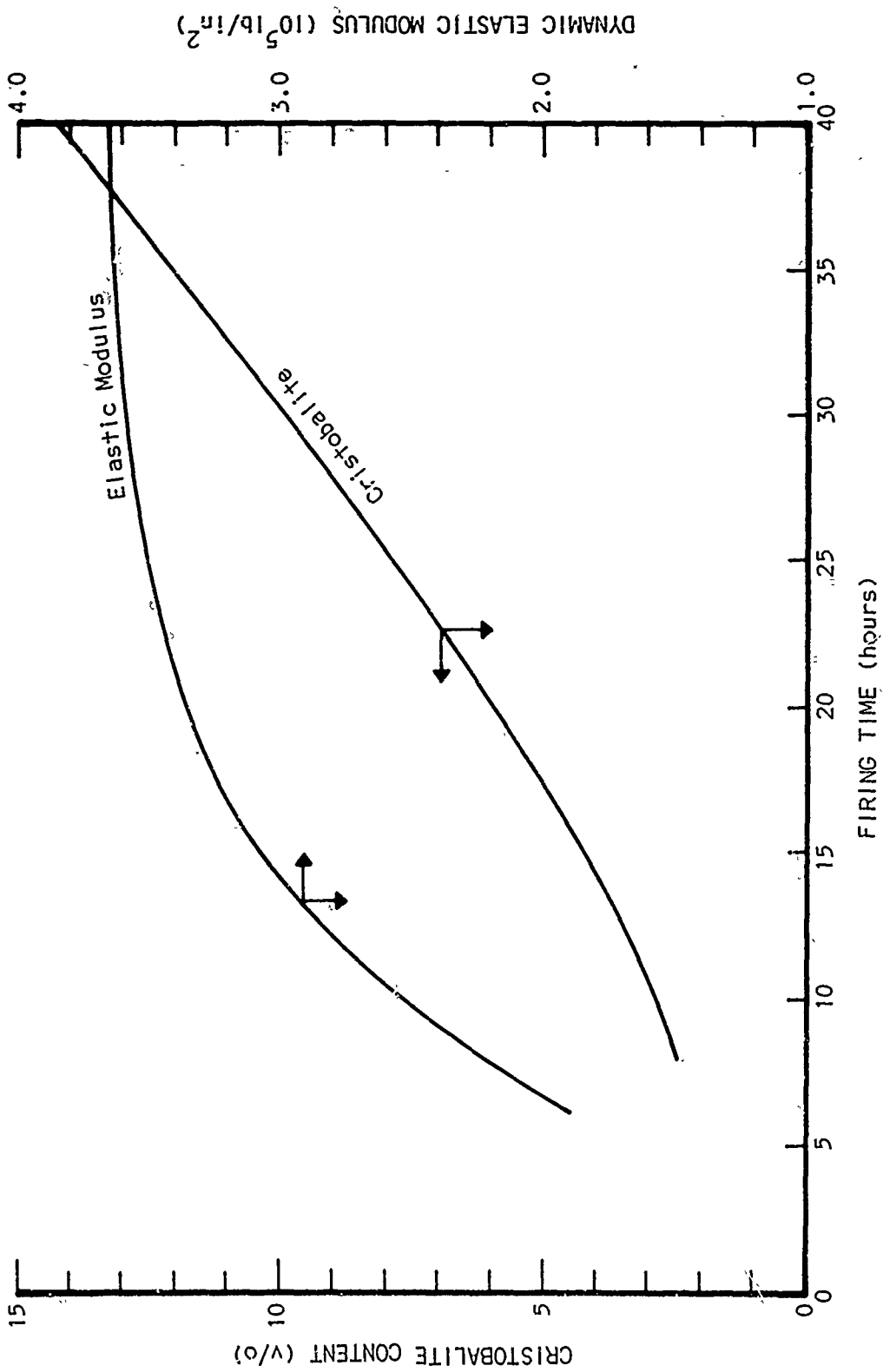


Figure 4. Cristobalite Content and Dynamic Elastic Modulus vs Time Sintered at 2200° F for High Purity Fused Silica Foam of Nominal 25 lb/ft³ Density.

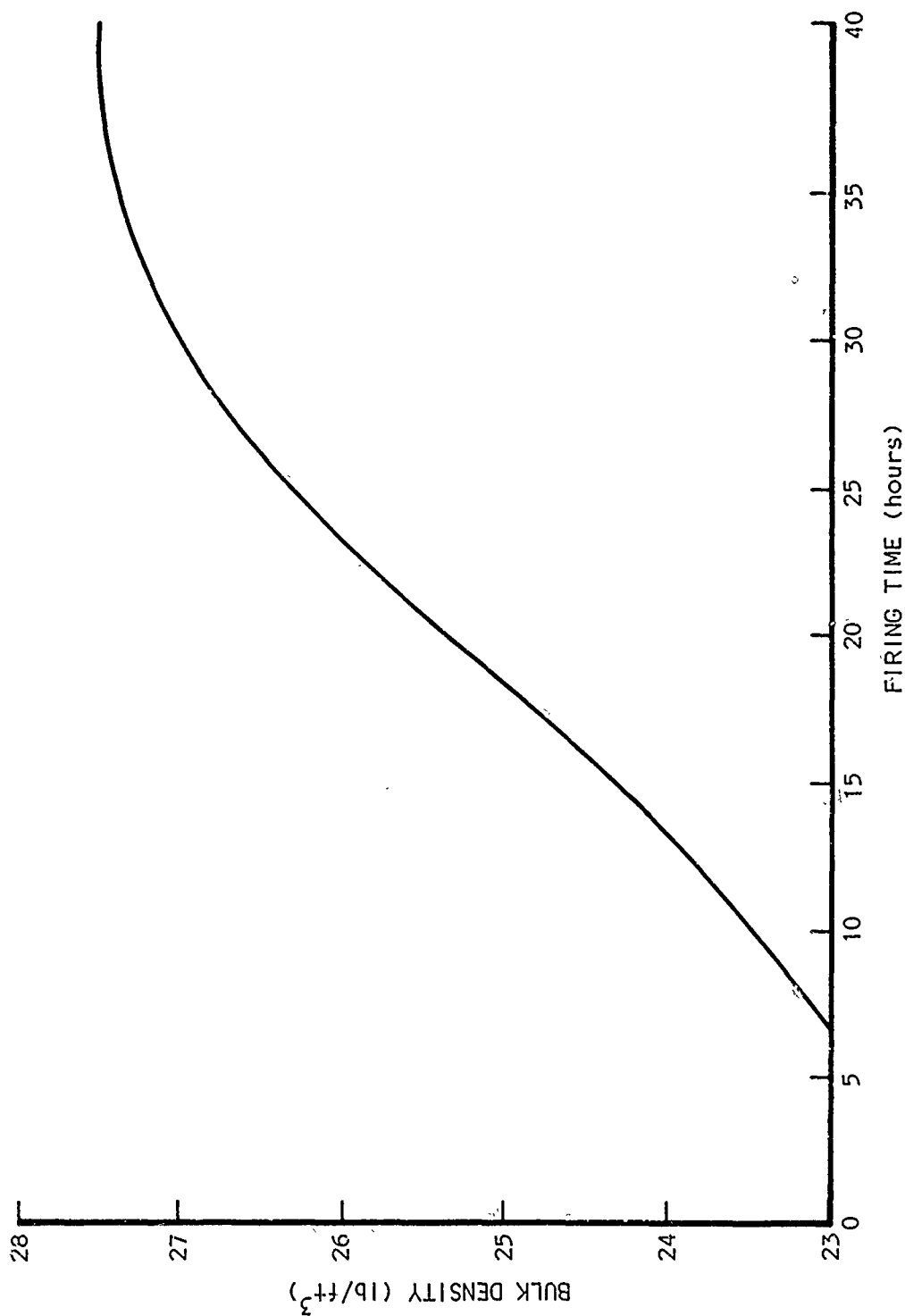


Figure 5. Bulk Density vs Time Sintered at 2200° F for High Purity Fused Silica Foam of Nominal 25 lb/ft³ Density.

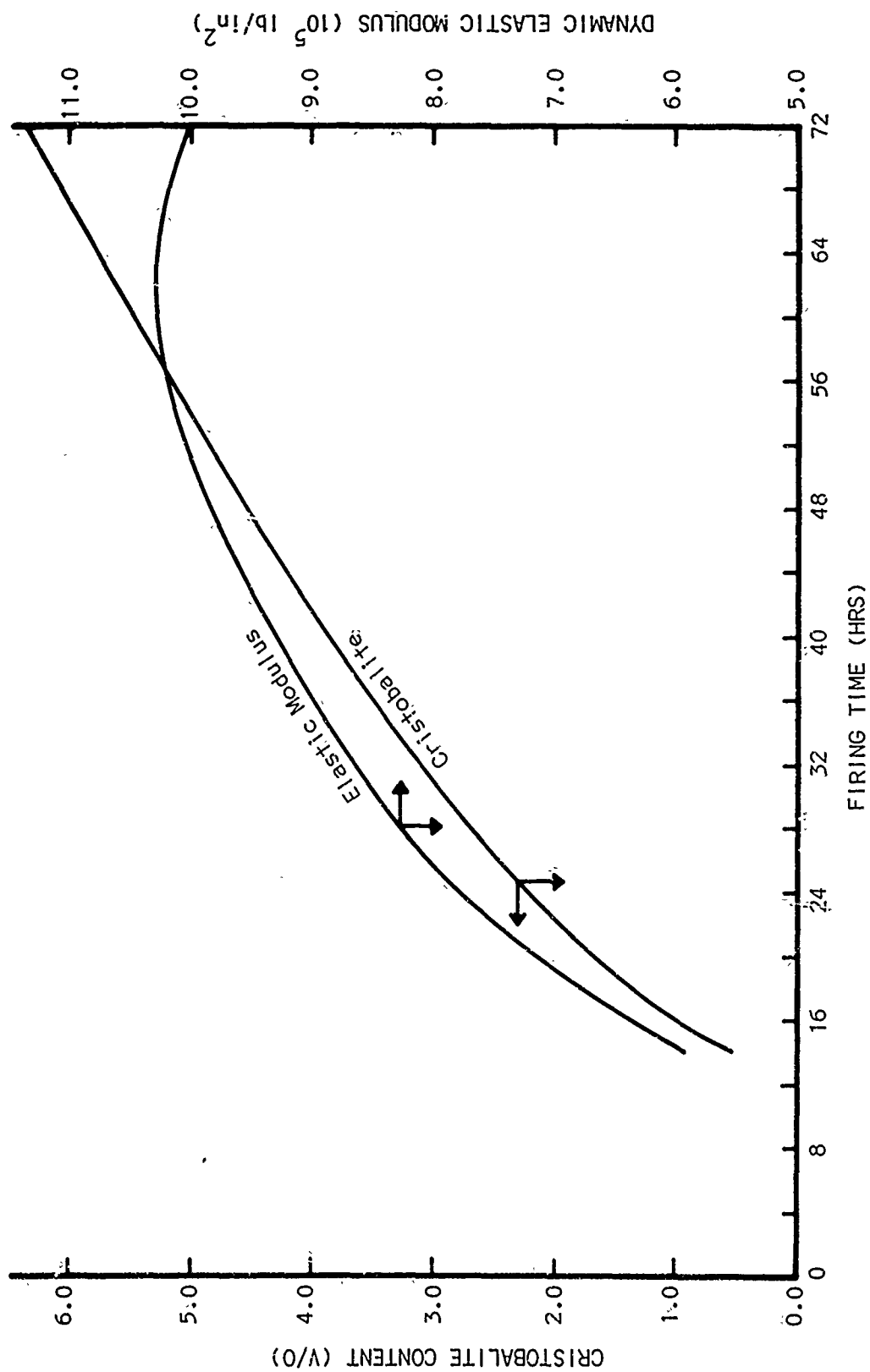


Figure 6. Cristobalite Content and Dynamic Elastic Modulus vs Time Sintered at 2200° F for High Purity Fused Silica Foam of Nominal 45 lb/ft 3 Density.

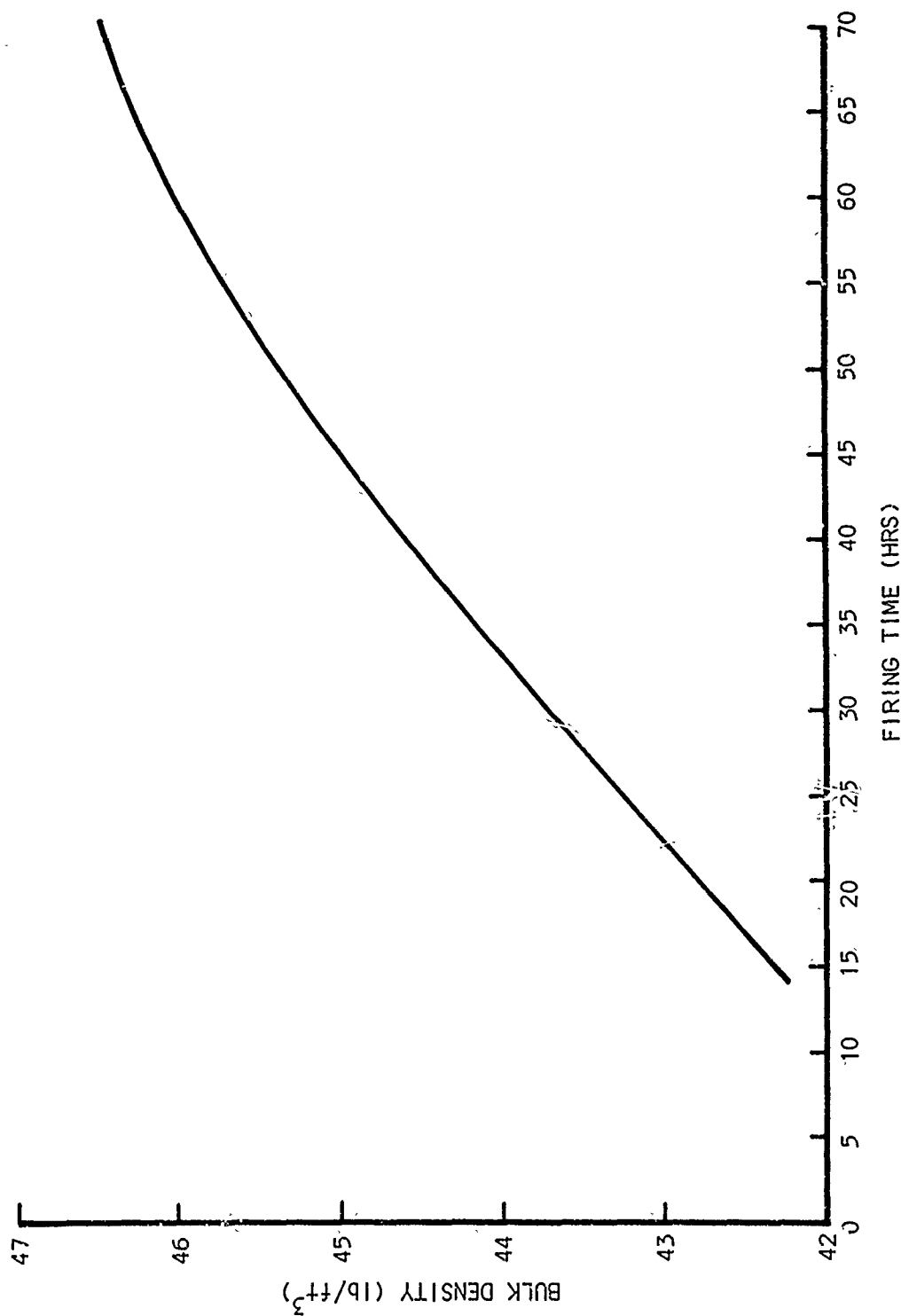


Figure 7. Bulk Density vs Time Sintered at 2200° F for High Purity Fused Silica Foam of Nominal 45 lb/ft³ Density.

c. Fiber and Whisker Reinforced Fused Silica Foams

A study was begun to determine the effect of fiber and whisker materials on high purity foams. Previous work with alumina and zirconia fibers and silicon carbide whiskers in slip-cast fused silica, and in fused silica foams, both prepared from arc fused material had shown some promise, but strength increases were offset by greatly increased devitrification rates 2,3/. It was hoped that the reduced devitrification rate of the high purity material would permit increased sintering. For this study boron nitride fibers, pyrolitic graphite fibers with a silicon carbide coating, and silicon carbide whiskers were selected.

Before work could begin on incorporating fibers or whiskers in a foam, two brief studies were necessary. First a spectrographic analysis was made on each of the whisker and fiber materials. In addition a survey of the variables in the foaming process was necessary to produce a consistent low density foam to use with the whisker and fiber reinforcements.

Other contract work^{*} had shown that boron nitride fibers contained small amounts of sodium which could be removed by boiling in water or by leaching with hydrochloric acid.

A spectrographic analysis of the pyrolitic graphite fibers showed traces of magnesium, iron, zirconium, boron and calcium. All traces of these elements with the exception of boron, were removed by leaching in hot concentrated hydrochloric acid.

Two batches of silicon carbide whiskers were checked. One batch had been fired in air at 2200° F for one hour to form a surface layer of silica on the whiskers. The other batch was as received from the manufacturer. Both batches showed significant amounts of calcium. The oxidized whiskers showed

^{*}Georgia Tech Project A-1001.

traces of boron, aluminum, magnesium, iron, vanadium, copper, sodium, titanium, nickel, and chromium. The as received material showed traces of boron, magnesium, iron, aluminum, copper, and nickel. Leaching with hot hydrochloric acid and with boiling aqua-regia had little effect on impurities. An x-ray diffraction examination of the whiskers showed small amounts of crystalline impurities tentatively identified as calcium-silicate hydrates.

Presently, a systematic study of five variables in the foaming process is being made. The variables under consideration are the amounts of Cab-O-Sil[®], detergent, hydrochloric acid, and make-up-water in the foam, and the whipping time. The Cab-O-Sil[®] is being used to increase the viscosity of the slip prior to foaming. The hydrochloric acid serves to stiffen the foam once whipping has begun. The make-up-water is necessary to supplement the low percentage of water present in the slip.

Through a matrix technique, the variables may be evaluated in terms of their effects on foam properties such as bulk density and elastic modulus. In addition, the technique should indicate the direction each variable should be changed to optimize any property considered. Due to the large number of foams needed, a conventional casting slip is being used for initial studies.

d. Slip-Cast Fused Silica Honeycomb

Thus far efforts to improve the strength of fused silica foams without increasing bulk density have not fully reached the contract design goals. An alternate approach to the fine pore foam would be a honeycomb structure with uniform void spacings. These void spacings would be oriented with changing radome wall shape so that the electromagnetic beams transmitted through the radome would pass through a minimum number of cell walls.

The low drying shrinkage and ease of release from plaster molds make fused silica an attractive material for slip-casting complicated shapes such as honeycombs.

A hexagonal close packed structure slip-cast from fused silica with circular voids would give a minimum bulk density of 13 pounds per cubic foot if all cylinders were tangent. However, considering circular voids $1/4$ -inch in diameter with cell walls 0.025-inch in thickness the bulk density would be about 35 pounds per cubic foot. A close packed hexagonal structure with $1/4$ -inch hexagonal voids and 0.025-inch cell walls would have a density of approximately 25 pounds per cubic foot.

Several fabrication techniques were considered for slip-casting a hexagonal close packed structure. All considered the use of removable cores. The cores would be removed either before or after drying. One method consisted of using a low melting wax which was removed during low temperature drying. A honeycomb section was fabricated by this technique. However, the fired structure had numerous cracks in the cell walls. These cracks were attributed to strains set up by shrinkage during drying. A second method was to place small rods of plaster in a hexagonal pattern within the female mold. After casting and before room temperature drying was complete the plaster cores were pushed out individually. This technique is of course, tedious and time consuming since great care must be exercised in pushing out the cores to prevent spalling the back surface.

The most satisfactory method was to locate plastic cylinders in a guide plate which in turn fitted into a plaster mold. (Right circular cylinders rather than hexagonal shapes were used only because they were more readily available.) This apparatus was sealed with a cover plate and fused silica

slip introduced into the system. After 7 hours casting time the mold was opened, the plastic cylinders pulled out of the mold, and the honeycomb disk removed. Figure 8 shows one such honeycomb section. This specimen had a bulk density of 53 pounds per cubic foot.

Several additional samples were fabricated by the same method. Three of these samples were crushed to determine compressive strength. Two of the samples had surface flaws and showed crushing strengths of 6400 and 7800 psi. The third sample had a much better surface and yielded a crushing strength of 10,800 psi.

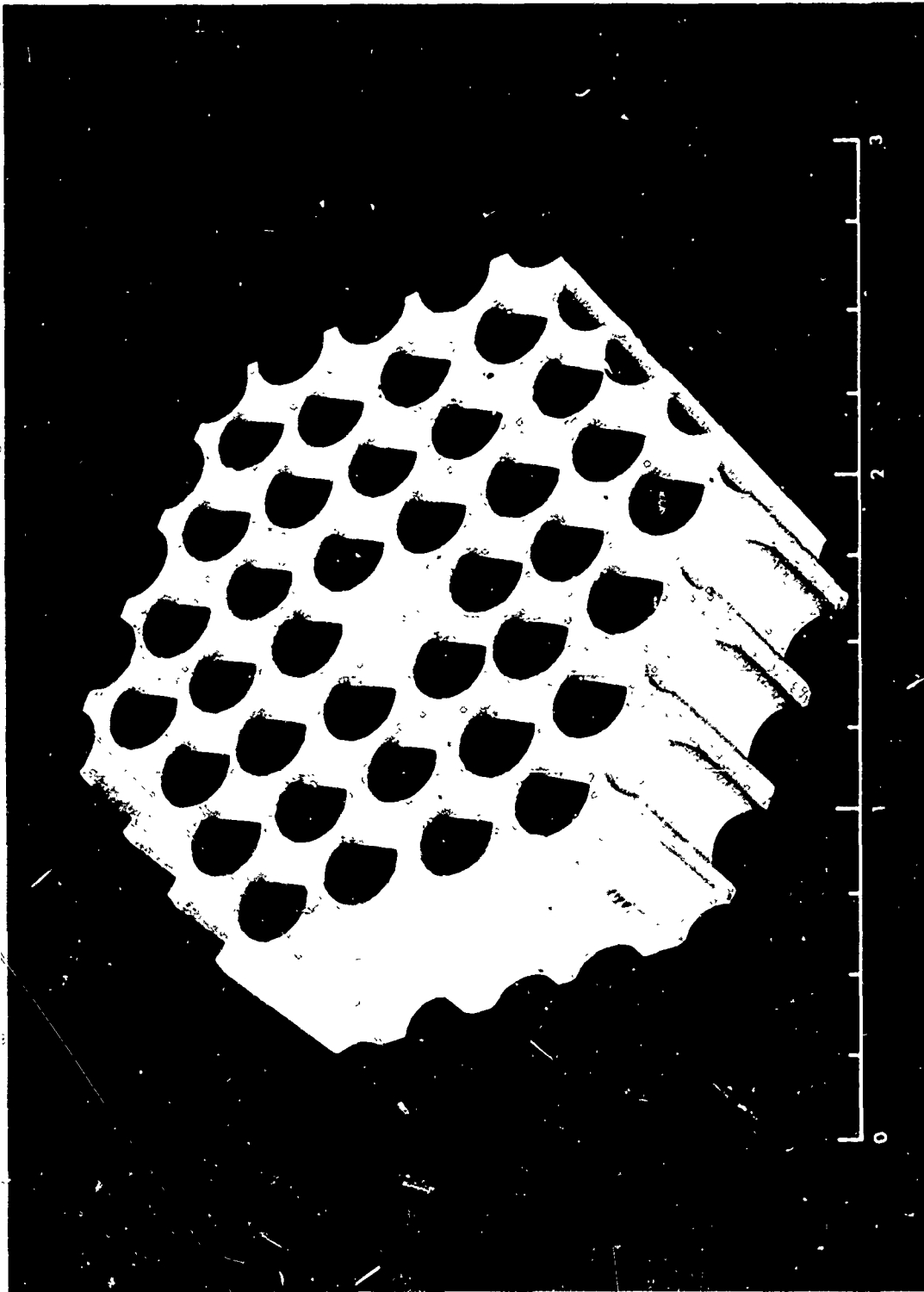


Figure 8. Section of Slip-Cast Fused Silica Honeycomb.

2. Development of High-Density, High-Strength Structures

a. Purity

Under this program a screening investigation was conducted to ascertain the most promising approaches to develop a significantly improved fused silica slip. Initial investigations considered two sources of starting materials.

1. A very pure amorphous silica produced by the steam pyrolysis of silicon tetrachloride.
2. A fused silica manufactured from very pure deposits of quartz used in the production of high quality transparent fused silica components.

Several materials are available which originate from the steam pyrolysis of silicon tetrachloride. One of these, Corning 7940 fused silica, is an ultra pure material available in a wide range of particle size distributions. The present price of this material is in excess of thirty dollars per pound. Another high purity material, Cabot Corporation's Cab-O-Sil[®] M-5, is priced at approximately eighty cents per pound, and is manufactured in quantities on the order of 5 to 10 million pounds per year. However, it is an extremely finely divided material. The particles are essentially spherical and sponge like (porous), as shown in Figure 9. A spectrographic analysis of this material is shown in Table X.

The work on producing a fused silica slip from fused material produced from very pure deposits of quartz has been deferred because this system is being investigated on a concurrent Georgia Tech research program*.

* Georgia Tech Project A-1001.

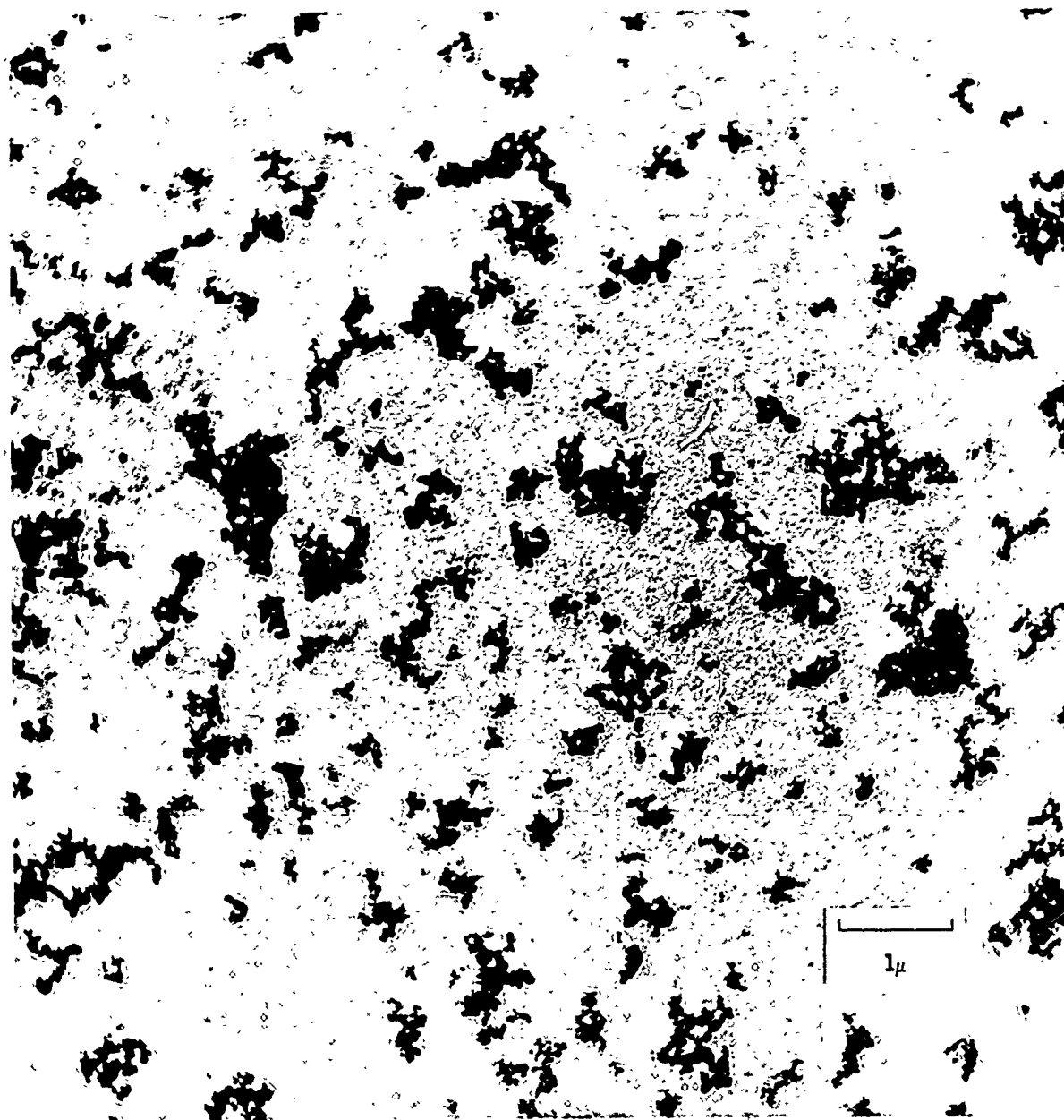


Figure 9. Electron Micrograph of Cab-O-Sil® M-5 Particles.

TABLE X
SPECTROGRAPHIC ANALYSIS OF M-5 CAB-O-SIL[®]

<u>Element</u>	<u>Quantity</u> (w/o)
Si	Remainder
Mg	0.002 +
Fe	0.0005
Al	0.0002

b. Particle Size Distribution

In view of the price and availability of Cab-O-Sil[®], this material seemed to be distinctly the best choice as a starting material for the improved fused silica slip studies. However, there is one disadvantage to Cab-O-Sil[®] M-5. It is essentially a monofraction with a mean particle diameter of 0.012 micron and must be consolidated into particles about 0.1-inch or so in diameter and wet ball milled to produce a slip with a log-normal particle size distribution ranging downward from 50 microns.

The following methods were considered to densify and coalesce the Cab-O-Sil[®] M-5 material so as to obtain larger particle diameters.

1. Direct sintering of loose powder.
2. Sinter, disperse sintered product in water, dry, and resinter.
3. Filter press from liquid slurry, dry, and sinter.

4. Compact "dry powder"* under pressure with subsequent sintering.
5. Dry, water dispersion and sinter.
6. Extrusion from Cab-O-Sil®/water paste with subsequent sintering.
7. Spray drying.

The results of our investigations have shown that dry pressing, followed by drying and sintering; and extrusion of a silica "spaghetti" followed by drying and sintering are two feasible methods for achieving the required densification of Cab-O-Sil® M-5. Other techniques involving direct sintering of loose powder; sintering, dispersion in water, drying and resintering; filter pressing from slurry, drying and sintering; gelling with water, drying and sintering; and spray drying of water slurry, failed to give suitable material for grinding. These latter processes produced friable, porous materials and/or unacceptably high levels of crystallinity after sintering.

The two successful methods for producing a suitable ball mill charge from Cab-O-Sil® deserve further description. With dry pressing, Cab-O-Sil® powder is placed in one-pint plastic food freezer bags, then pressed in a 4-inch square tile die to a pressure of about 3200 psi (50,000 lbs applied load). The purpose of the plastic bag is to prevent contamination of the silica by the steel die and to facilitate handling of the fluffy powder. Force on the die is released slowly, and the pressed "cake" is removed. After the plastic

* Sufficient absorbed and/or adsorbed water is present on/in the particles to act as a binder/lubricant.

bag is cut away the silica is recovered as thin sheets or laminae, one to two millimeters thick. Each pressing cycle yields about 15 grams of cake. About twice this amount of silica can be pressed if air is evacuated from the plastic bag, but the extra yield is not commensurate with the additional effort required to remove the air from the bag. One to two pounds of pressed cake is collected in a silica firing boat, dried and fired at 2200° F for 3-1/3 hours. The resulting mill feed is in the form of translucent platelets, approaching theoretical density. These platelets typically have a cristobalite level of 0.0 to 0.6 v/o.

Extrusion of a silica "spaghetti" is the second method which can produce a satisfactory ball mill feed. Considerable effort has been devoted to development of this method because it offers the possibility of being readily scaled up to quantity production. To avoid contamination of the silica by metallic impurities, a hardwood die was used for early extrusion experiments. It proved unsatisfactory because the plunger could not be prevented from seizing in the die. Extrusion was continued using a steel punch and die with a hardwood plug through which the "spaghetti" was extruded. The optimum composition of the extrusion mixture was found to be 30 w/o Cab-O-Sil[®] and 70 w/o distilled water. No wetting agents or other adulterants were used, since high purity of the extruded mixture was a major objective. Test quantities of "spaghetti" were dried, then fired at 2200° F for 3-1/3 hours to achieve densification. The resulting mill feed was in the form of short cylinders, about one millimeter in diameter, very much like rice in appearance. Typical cristobalite content of this material after firing was 0.0 to 0.6 v/o.

Materials that are suitable for comminution by ball milling to fused silica slips can be produced by both the extrusion and dry pressing methods.

In both cases the cristobalite content is on the order of 0.6 per cent or less; it is desirable that this quantity be as low as possible in mill feed used to produce improved silica slips. Both processes can be scaled up to pilot quality and ultimately to production quantity levels without prohibitive expense and difficulty.

Experimental quantities of high purity fused silica slip were made by grinding the feed in one gallon ball mills. The mill and grinding media were usually 99.6 per cent alumina. Alumina has a higher hardness than conventional mullite type mills and grinding balls; it was therefore preferentially used to avoid contaminating the slip with crystalline silica abraded from the mill and balls.

A quantity of extruded feed (about 2 pounds) sufficient for an experimental mill of high purity silica slip was prepared. After sintering, this material contained a very high level of cristobalite, and was unsuitable for grinding. The origin of the cristobalite was subsequently traced to contamination of the extruded material during drying.

Meanwhile, six experimental batches of high purity silica slip were prepared from dry pressed and fired mill feed and characterization studies were conducted. Each experimental batch yielded approximately one quart of finished slip. (About half the volume of the one gallon mill is occupied by grinding balls, one-quarter by slip and one-quarter is empty space.) Grinding times of 18, 24, 27, and 48 hours were used. The slips had properties similar to conventional fused silica slips and could be cast by conventional techniques without difficulty. Pertinent properties are shown in Table XI, along with those of a good batch of commercial fused silica slip, Glasrock® Batch 561-B.

TABLE XI
PROPERTIES OF SEVERAL FUSED SILICA SLIPS

<u>Slip</u>	<u>pH</u>	<u>Apparent Viscosity</u> (cp)	<u>Per Cent Solids</u> (w/o)	<u>Grinding Time</u> (hr)	<u>Residual Cristobalite</u> (v/o)
1	3.55	140	77.8	48	0-0.6*
2	3.75	121	79.3	27	0-0.6
3	3.86	110	80.1	24	0-0.6
4	4.05	105	77.8	24	0-0.6
5**	4.10	74	77.6	18	0-0.6
6***	3.70	159	71.8	18	0-0.6
Glasrock® Batch 561-B	4.50	114	83.1	--	1.5-2.0

* Cristobalite content of mill feed.

** Cab-O-Sil® M-5 ground in mullite mill.

*** Cab-O-Sil® M-7 ground in alumina mill.

The first four experimental slips were made from Cab-O-Sil® M-5 and ground in alumina mills. These slips were intended to define a suitable grinding time and to demonstrate that slips with satisfactory reproducibility could be made. Experimental Slip No. 5 was prepared in a mullite ball mill, but otherwise was similar to those just described. The slip obtained had the expected particle size, viscosity, and pH characteristics. The devitrification rate of slip ground in the mullite mill has been found somewhat higher than for slip ground in high-alumina mills. This effect was expected since the less tough mullite mill should wear more than the alumina mill and thereby

yield some contamination of the slip. Since large batches of silica slip are generally ground in mullite mills, Slip No. 5 was intended to determine whether significant deterioration in fired properties would result from such grinding.

Cab-O-Sil[®] M-7 is also a readily available material and is represented by the manufacturer as being identical to M-5, except that it has been partially agglomerated to a bulk density of about twice that of the M-5 powder. A sample quantity of M-7 was obtained and experimental Slip No. 6 produced from this material using an alumina mill. After pressing and firing, the mill feed had a slight yellow coloration, but spectrographic and x-ray analysis failed to identify any contamination responsible for this off-color. The slip had the expected particle size, viscosity and pH. If M-7 is found to be a satisfactory starting material for high-purity slips, it would be preferred over M-5 because its higher bulk density facilitates consolidation into mill feed.

Particle size distributions measured with a Coulter Counter[®] are shown in Figures 10, 11, and 12 on a mass and count basis. In these and subsequent figures, data representing the aforementioned Glasroc[®] Batch 561-B are shown for comparison. Details of the particle measurement technique have been described elsewhere 4. It should be noted, however, that direct counts are obtained only for particles with diameters in excess of two microns. Size distributions on a count basis are obtained by an extrapolation technique based on the assumption of a log-normal distribution. Such an assumption is justified for conventional fused silica slips.

Firing studies were conducted on the experimental slips. In these studies two 3/4-inch diameter bars were cast from each slip and dried. The bars were fired together in an electric furnace at 2200° F for 2 hours; then volume per cent cristobalite, modulus of elasticity, porosity, and bulk and theoretical

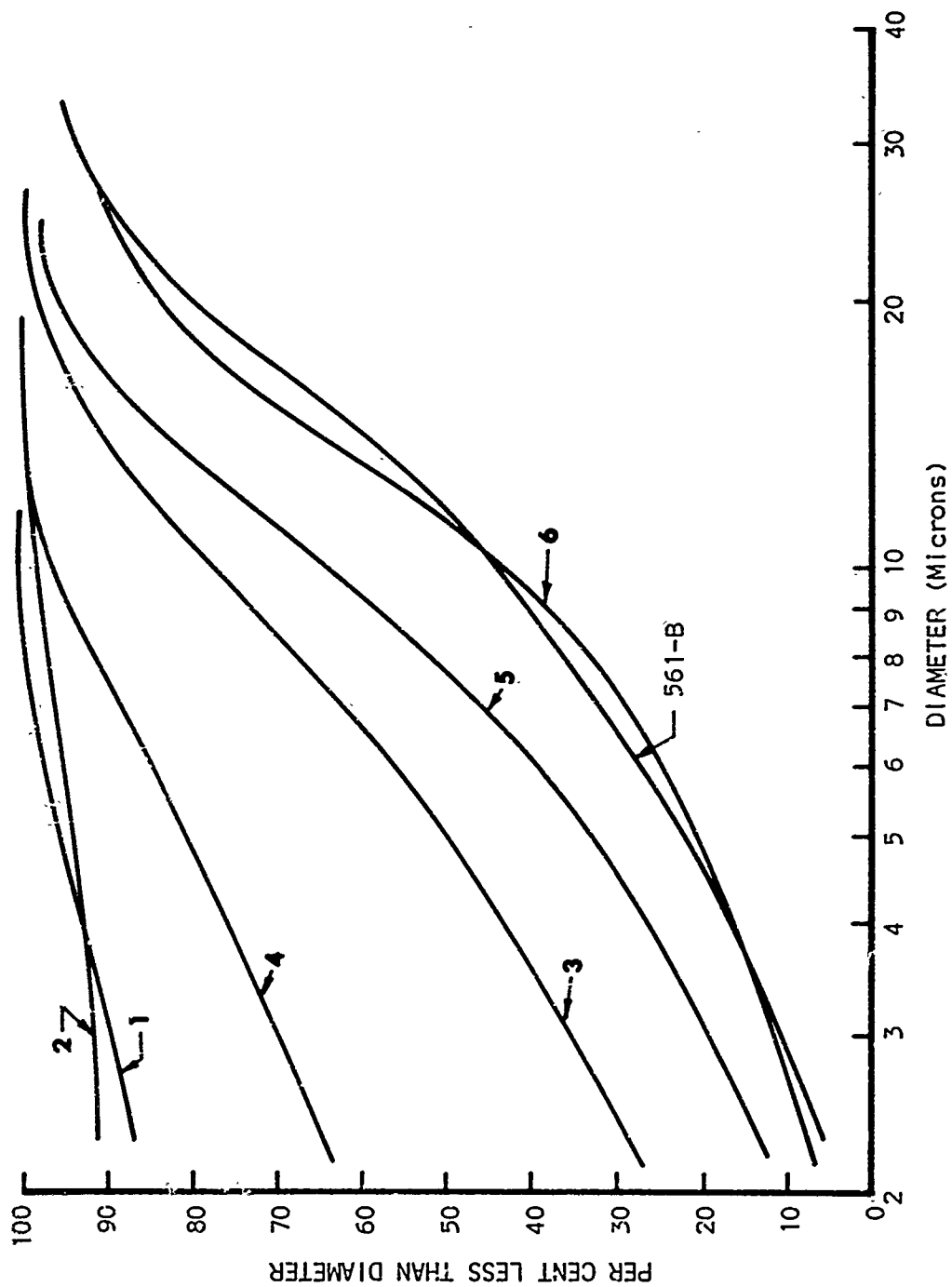


Figure 10. Mass Basis Particle Size Distributions of Glasrock® 561-B Slip and Six Experimental Cab-O-Sil® Slips.

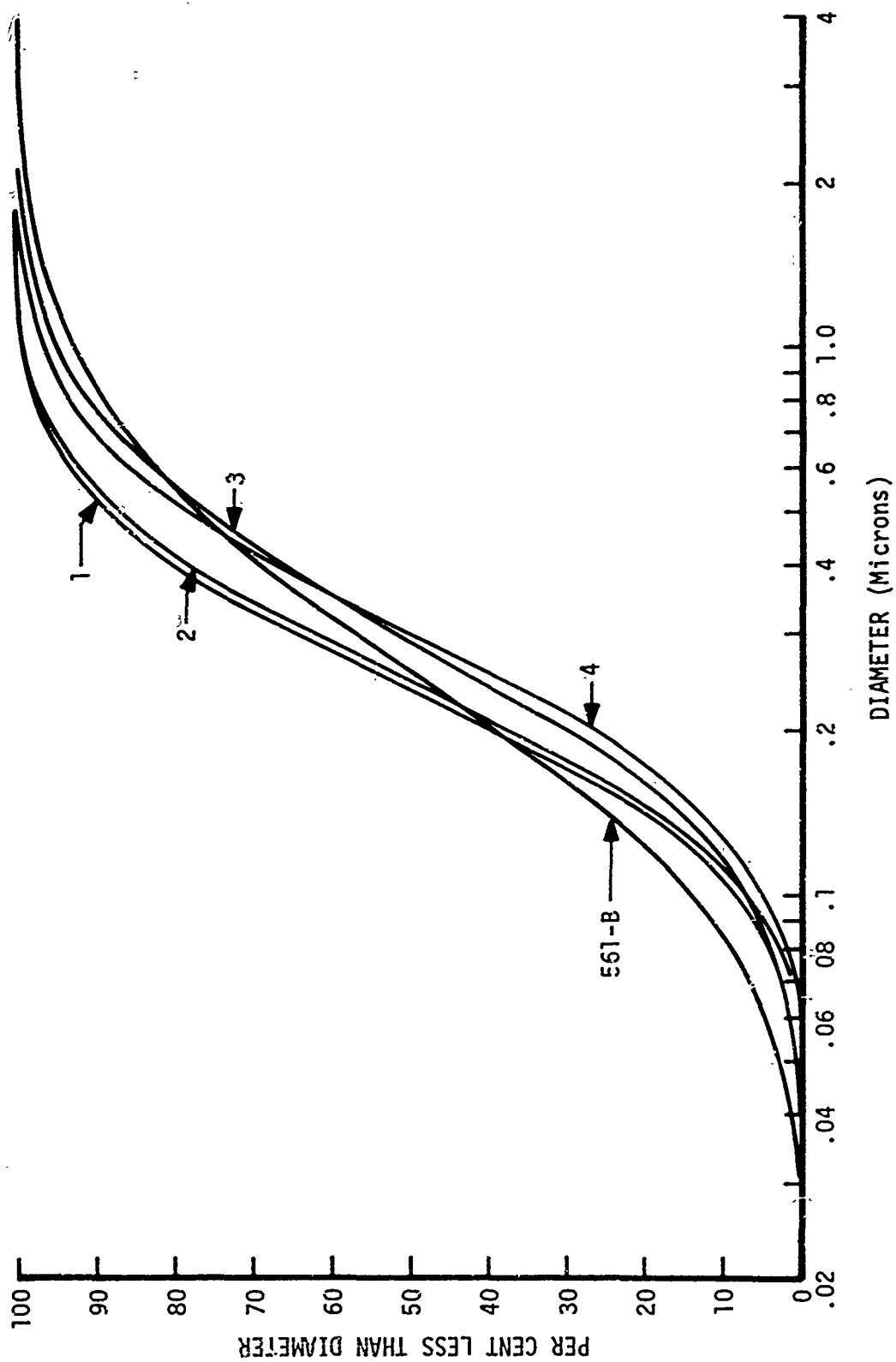


Figure 11. Count Basis Particle Size Distributions of Glasrock® 561-B Slip and Four Experimental Cab-O-Sil® Slips.

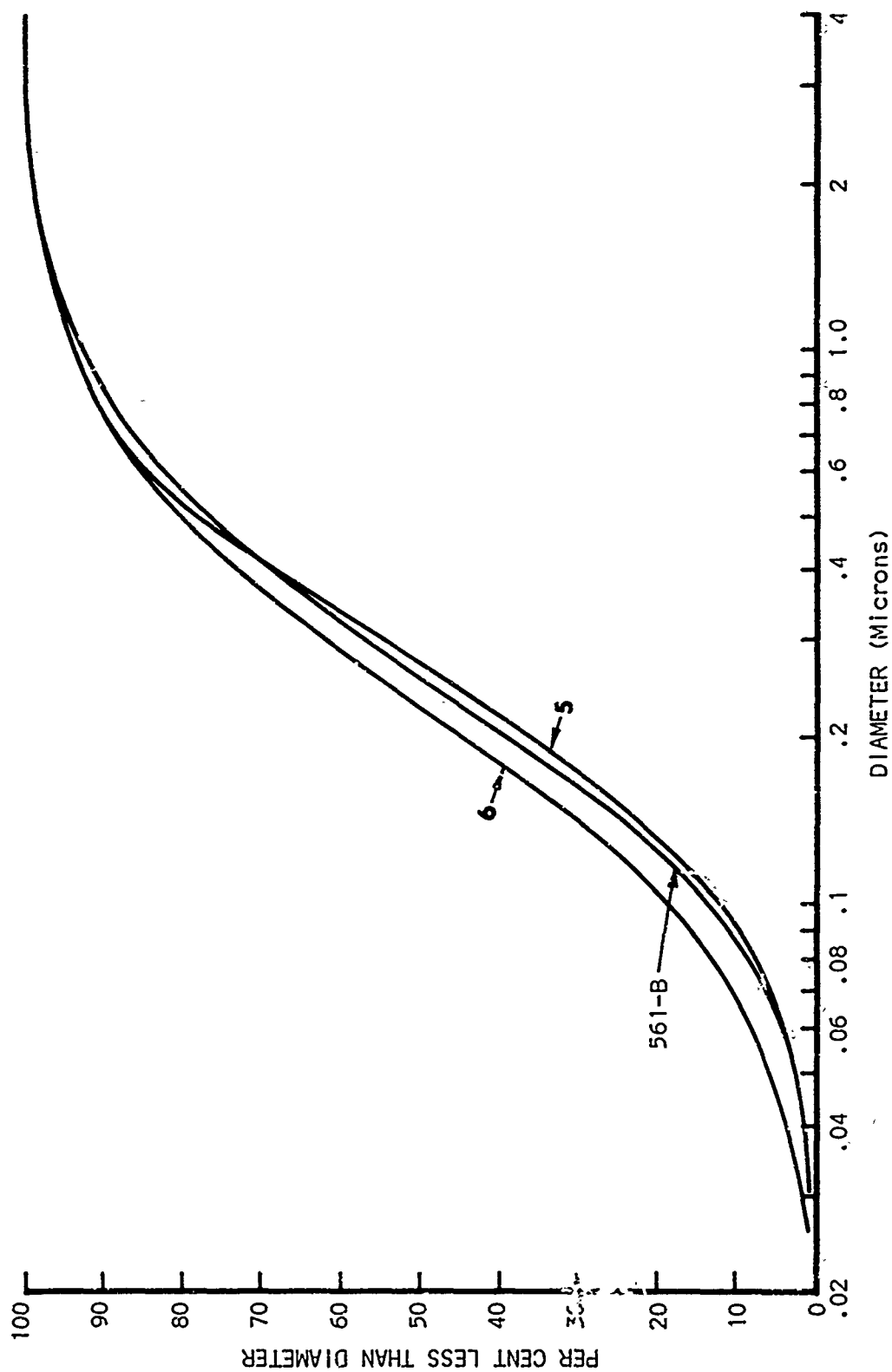


Figure 12. Count Basis Particle Size Distributions of Glasrock® 561-B Slip and Two Experimental Cab-O-Sil® Slips.

densities were measured. The bars were then fired under the same conditions for another increment of time, and all measurements repeated. This procedure was carried on until the bars broke up from excessive devitrification, and yielded an extensive body of data as a function of firing time at 2200° F. This temperature is used in most fused silica firing studies at Georgia Tech because it gives a convenient compromise between a fast sintering rate and adequate control. The most revealing of these data are shown in Figures 13 and 14 for the experimental slips and the Glasrock fused silica slip mentioned previously.

Figure 13 shows cristobalite content versus sintering time at 2200° F. The pressed and sintered Cab-O-Sil® M-5 used to produce Slip 1 contained small white spheres which were identified as cristobalite. About 50 of these spheres were removed manually from approximately two pounds of mill feed. At the center of each was a small, dark-colored nucleus; the nuclei were found to contain principally carbon, iron, magnesium, and chromium. It is believed that these foreign nuclei were in the original Cab-O-Sil® because the feeds for Slips 2 through 5 which were taken from different bags of Cab-O-Sil®, contained very few such cristobalite spheres.

Figure 14 shows elastic modulus versus sintering time at 2200° F. The elastic modulus was measured by a sonic technique 5/. The elastic modulus curve for Glasrock Batch 561-B is typical of a large number of conventional slips investigated by this method. The experimental slips reached a maximum elastic modulus of about 8 to 9.6 million psi, higher by a factor of two than conventional slips. Slip No. 6 (Cab-O-Sil® M-7) showed exceptionally low rates of sintering and cristobalite formation. After 60 hours of firing at 2200° F, its elastic modulus reached a value of 7.7×10^6 psi at a cristobalite

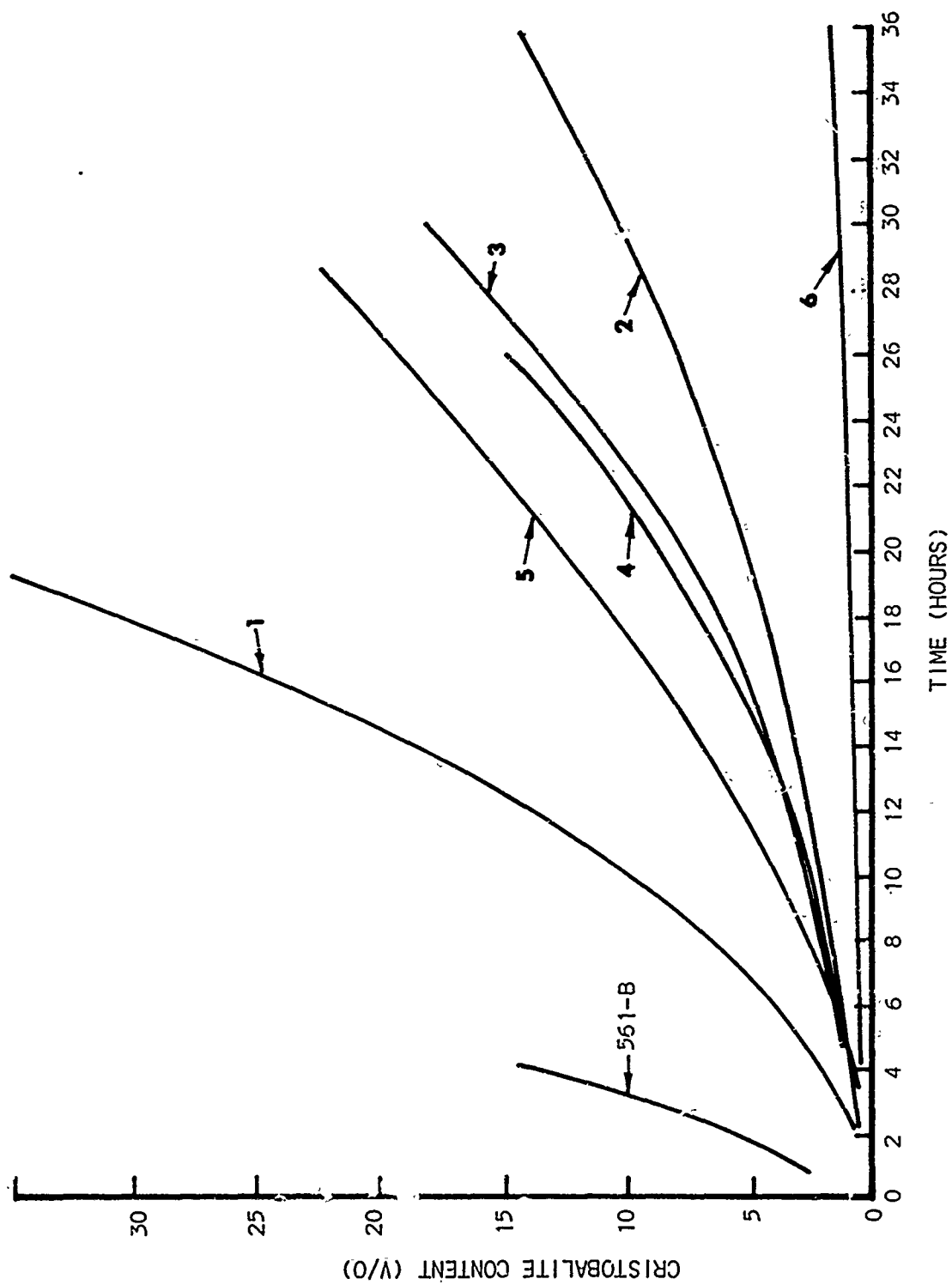


Figure 13. Cristobalite Content vs Sintering Time at 2200° F for Experimental Fused Silica Slips.

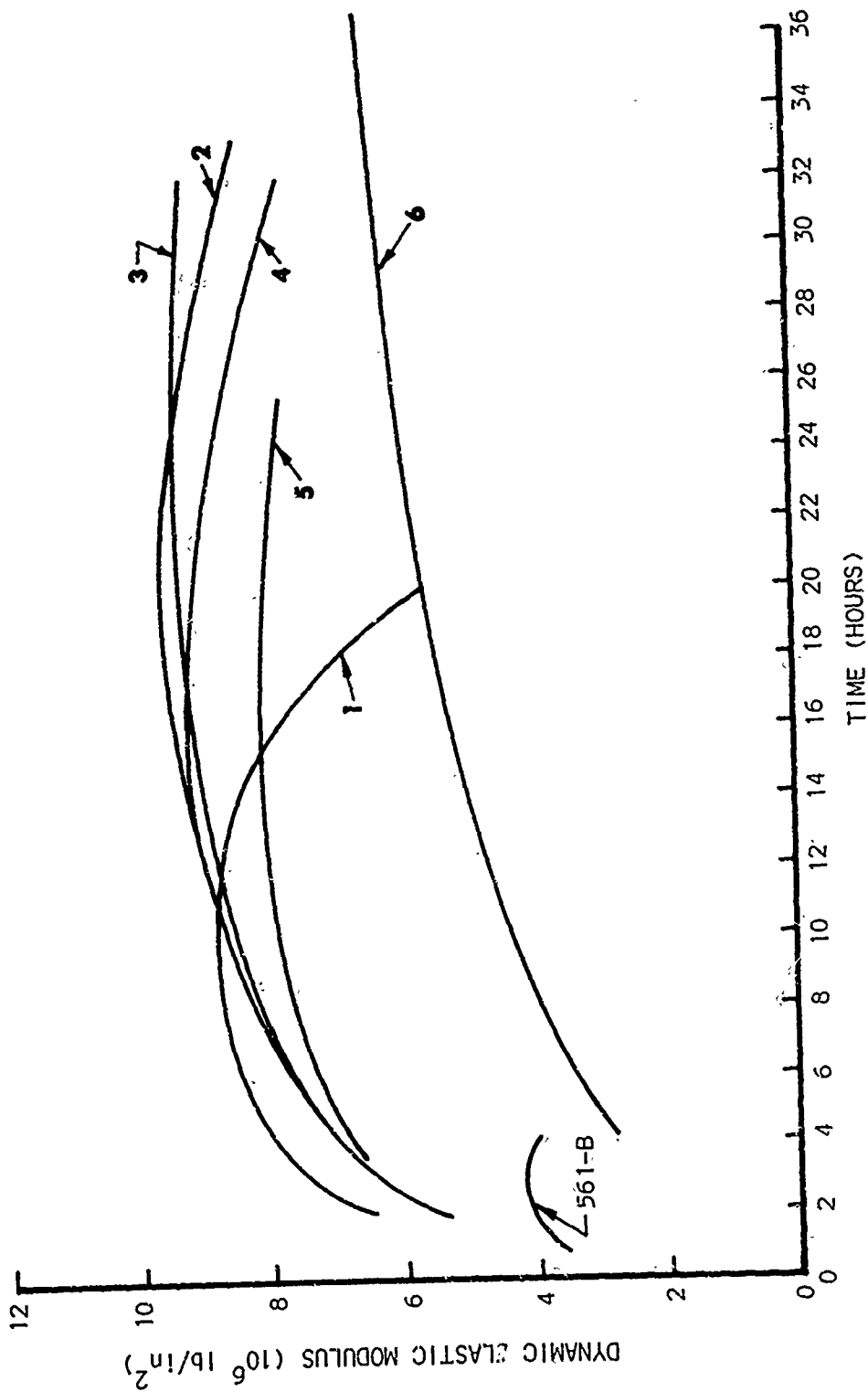


Figure 14. Elastic Modulus vs Sintering Time at 2200° F for Experimental Fused Silica Slips.

content of only 4 per cent. The peaks are seen to be rather broad so that further improvement might be achieved by adjustment of sintering temperature.

To assess further the casting characteristics of silica slips produced from Cab-O-Sil[®], several small cones were cast from the remnants of M-5 slips ground in alumina mills. Wall thicknesses of these cones ranged from 0.033 to 0.058 inches. To successfully remove the cones from their molds, the tips were dried with a stream of compressed air directed toward the tip with a hypodermic needle. Other drying techniques caused the skirt to dry more rapidly than the tip, and circumferential cracks developed because of uneven shrinkage. Cracking was observed in some cases upon firing of the thin-wall cones. Based on previous experience, this indicates that the slips have somewhat smaller particle sizes than optimum.

Attempts to extrude silica "spaghetti" through an auger driven pug mill were unsuccessful because of the unfavorable rheological properties of Cab-O-Sil[®]/water mixtures.

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SECTION III

DISCUSSION

The all inorganic filament wound system developed under Air Force Contract AF 33(615)-3330 does not appear to be capable of a very wide change in bulk density with minor changes in winding circuits and patterns.

Variations in winding patterns and in the number of circuits per pattern did not reduce the density of inorganic filament wound structures sufficiently to allow their use as the core portion of an A-sandwich radome. Use of such structures can only be accomplished if the matrix is sufficiently porous to reduce the total density of the filament wound composite. A small decrease in apparent porosity and bulk density was achieved at winding angles of 45 degrees and 32-1/2 degrees as opposed to 57-1/2 degrees. The significance of this difference is difficult to define because of the large scatter in data. The number of circuits per pattern apparently had very little effect on the bulk density of the finished item.

The highest tensile strength was obtained in the specimens wound at 57-1/2 degrees. The reason for this is two-fold: (1) the higher density and, (2) the filament-matrix shear failure mode. On the 1/2-inch wide specimens there were longer lengths of uncut filament at this winding angle than on the other two winding angles. This resulted in a greater surface area for filament to matrix bond. Hence, it required a greater stress to fail these specimens.

The phenomenon of decreasing tensile strength with increasing heat-treatment temperature has been fully discussed in AFAL TR 67-65 1/. The decrease in tensile strength with temperature of the specimens shown in Table III is probably due to the caramelizing and subsequent oxidation of the starch oil size. The silica particles are in contact with the fibers but are

not yet bonded by sintering action. Any slippage in the system then allows abrasion of the fiber surface.

One method of density reduction is to incorporate an organic carrier filament or tape along with the inorganic filament or tape. The organic carrier becomes saturated with the matrix material and provides intimate contact with the inorganic fiber. Upon heat treatment the organic carrier burns out leaving a porous structure.

The use of cotton gauze as the carrier and burn out material did not produce low density composites of the strength level desired. The low modulus of rupture obtained can be attributed partially to the high level of cristobalite in those specimens sintered at 2200° F. The cause of the rapid devitrification was due to mineralizers from the cotton gauze. These mineralizers were present either in the cotton structure or on the surface in the form of a size or finish applied to the gauze. The reason for the low strength of those specimens heat treated at 1800° F is that insufficient sintering action occurs at this temperature to produce a strong particle to particle bond.

The washing of the cotton gauze demonstrated that all but trace elements of alkali impurities could be removed from the cotton. The trace elements left had very little effect on the devitrification of the composite. Therefore, this technique offers a method of producing a high purity uniform pore fused silica foam. The values for modulus of elasticity and modulus of rupture of foams made with fused silica slip and cotton gauze as shown in Table VII are in good agreement with the values predicted by Poulos ^{2/} for slip-cast fused silica of this density and having a bulk cristobalite content of 5 to 11 per cent. The foams made with the 58-40-2 binder and cotton gauze have an elastic modulus and modulus of rupture an order of magnitude lower

than that predicted for slip-cast fused silica materials of the same density. However, the cristobalite content of these materials was approximately 3 per cent. It is expected that sintering of these materials to a cristobalite content of about 8 to 9 per cent would bring the elastic modulus and modulus of rupture up to or would exceed the values predicted by Poulos 2/.

The modulus of rupture increases that were noted over those of previous specimens prepared with the unwashed gauze were due to the fact that the previous specimens were almost completely devitrified. Although cristobalite measurements were not made on the earlier samples their appearance indicated a very high percentage of cristobalite. Experience has shown that maximum elastic modulus and modulus of rupture for porous fused silica of 25 to 95 per cent of theoretical density occurs, depending on density, when the cristobalite content is between 5 and 11 v/o. The higher the density the lower the amount of cristobalite that can be tolerated without detriment to the elastic modulus and modulus of rupture.

Reinforcing the cotton gauze fused silica slip composite by filament winding alternate layers of cotton gauze and fused silica roving did not result in improving elastic modulus and modulus of rupture over that expected for a porous fused silica of the same density. The fused silica roving actually resulted in increasing the elastic modulus and modulus of rupture of the porous fused silica-cotton gauze composite. However, the amount of 100 per cent dense fused silica roving required for the reinforcement added to the total weight of the composite gave a final structure which was no stronger than a slip-cast fused silica structure of the same density.

The most promising materials for an A-sandwich core of an all silica radome at this point appears to be an ultra-pure foamed fused silica. Ultra

high purity fused silica foams can be sintered for much longer periods of time without excessive formation of cristobalite, thus extending the useful life of such a foam. The longer sintering period also results in an increase in elastic modulus over that of commercial fused silica slips. Although the G.E. fused silica foam of nominally 25 lb/ft³ density devitrified to 14 v/o cristobalite after 40 hours of firing it had reached an elastic modulus of 380,000 psi. The equation developed by Poulos 2/

$$E = 1,740,000 \frac{\rho}{164.0 - \rho} \quad (1)$$

would predict an elastic modulus of only 313,000. A higher density fused silica foam prepared from the Aeroceram slip developed only 4 v/o cristobalite after 62 hours of firing. The density of this foam was 46 lb/ft³ and it had an elastic modulus of 1,040,000 psi. Equation (1) would predict an elastic modulus at this density of only 678,000 psi. This represents an increase of 1.5 times in the elastic modulus over the commercial fused silica foams used under Contract AF 33(615)-3445 2/.

The use of discontinuous fibers in fused silica slip has not progressed to the point where it can be said that they can improve the strength of slip-cast fused silica. In the past the difficulty has been in preventing devitrification of the silica and in reducing the porosity of the cast piece 2,3/. However, high purity silicas show promise in reducing devitrification, while porosity increases associated with fiber/whisker additions present no problems in foamed structures. Investigations on the incorporation of boron nitride fibers, pyrolytic graphite fibers, and silicon carbide whiskers into foamed fused silica will be continued.

The use of a honeycomb structure rather than a foam appears promising due to the much higher strengths that can be obtained with oriented pore structures. The use of a honeycomb or oriented pore structure also allows better control of dielectric properties. The drawback to using ceramic honeycombs in A-sandwich radome construction has been the difficulty in forming the honeycomb. Although slip-casting of honeycomb structures from other ceramic oxides has proved impractical from the standpoint of mold release the magnitude of this problem with fused silica should be considerably less. The ease of mold release with fused silica and the technology of slip-casting fused silica should alleviate some of the problems experienced with other oxides.

The investigation of fused silica slips produced from Cab-O-Sil[®] synthetic amorphous silica has demonstrated that properties of the resulting bodies are substantially improved over conventional slip-cast fused silica. Thus, an important objective of the research program has been approached, and further improvement is expected as the material "system" is optimized.

Of the several methods considered for consolidating the finely divided Cab-O-Sil[®] into larger particles suitable for comminution to a slip, two have been shown to be feasible. Both require the application of mechanical pressure, in contrast to the unsuccessful consolidation techniques which depended on various heat treatments without mechanical pressure.

Large deviations among the curves in Figure 10 can be explained as follows. Most of the individual particles in a silica slip are less than two microns in diameter as shown in Figures 11 and 12. However, a large particle possesses mass equivalent to many smaller particles and thus will exert a very strong influence on the mass basis particle size distribution. The experimental slips (1 through 6) were seen to have a size distribution very similar to the

conventional slip (561-B) except that they contained fewer particles above one micron. The experimental slips were cast into 3/4-inch diameter test bars without difficulty. Characterization studies have shown improvement in the elastic modulus of test bars by a factor of two over conventional fused silica slip. The rate of devitrification of the improved slips is substantially reduced in comparison to conventional slips.

If Slip No. 1 is disregarded because it is known to have been contaminated with cristobalite in the mill feed, then Slip No. 5 is seen to have the highest rate of cristobalite formation among the experimental slips (Figure 13). This behavior was expected because a mullite mill was used in its preparation; however, its elastic modulus is seen in Figure 14 to have reached 8 million psi. The mullite mill did not seriously degrade the physical properties of slip prepared from Cab-O-Sil®.

Slip No. 6 (Cab-O-Sil® M-7) had not reached its peak elastic modulus after 72 hours of sintering at 2200° F, and showed a very low rate of cristobalite formation. Production of mill feed is made somewhat easier by the higher bulk density of the M-7 material, so that slips derived from Cab-O-Sil® M-7 deserve further investigation. At this point in the investigation, it appears likely that slips derived from the M-7 material will be at least as good as those produced from Cab-O-Sil® M-5.

Figure 15 shows a plot of elastic modulus as a function of cristobalite content for the experimental and conventional fused silica slips described earlier. In both conventional and improved slips, the elastic modulus reached a maximum at a cristobalite content of about 5 to 11 v/o. The improved properties achieved with high purity slips are believed to result from suppression of the nucleation and growth of cristobalite during sintering of

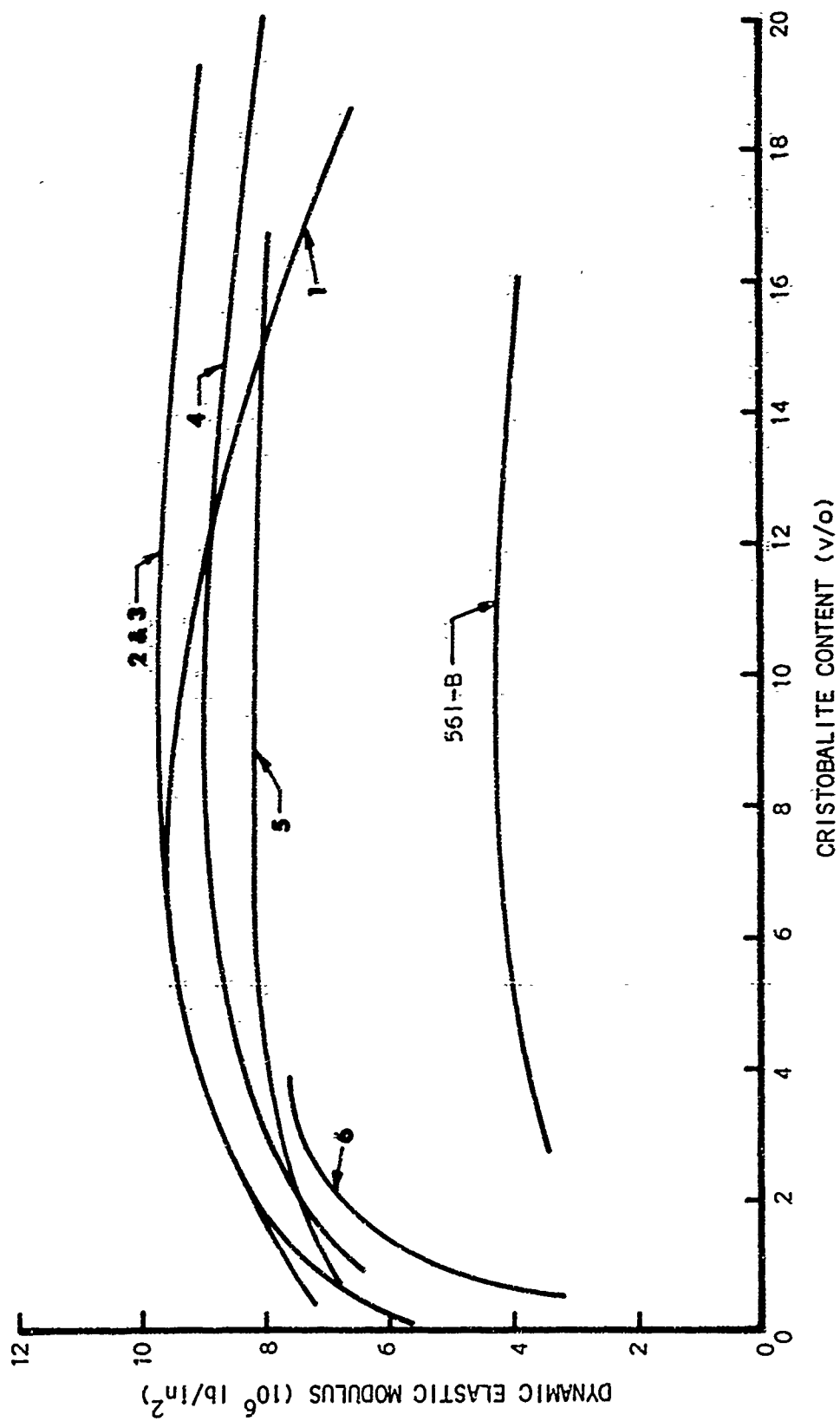


Figure 15. Elastic Modulus vs Cristobalite Content for Experimental Fused Silica Slips.

the cast bodies. After casting, the "green" bodies are fired at high temperatures (typically 2200° F) to fuse together particles in the packed structure. This operation develops strength by joining many small particles into a continuous piece, with a resulting decrease in porosity. However, cristobalite, a crystalline phase of silica, forms simultaneously at sintering temperatures, and upon cooling the cristobalite shrinks and causes microcracked flaws in the structure. Thus, the suppression of cristobalite growth reduces microcracking and the loss of strength associated with it. The fact that improved slips can be sintered much longer before reaching this cristobalite level, means that more complete sintering occurs with improved slips before the detrimental effects of cristobalite become important. Thus the maximum elastic modulus with high purity slips is found to be about twice that obtainable with conventional silica slips.

Inspection of Figure 14 reveals that the peak of elastic modulus with time is quite broad at a firing temperature of 2200° F in the experimental slips. This implies that firing time can be varied over a period of several hours without an important effect on the strength. In the same figure it is seen that a firing latitude of only about one hour is available with conventional slips. This short latitude is in large measure responsible for the choice of 2200° F as a "standard" firing temperature. Experience with conventional slips has shown that maximum strengths increase with higher sintering temperatures but the sintering time becomes very critical because the "peak" is much sharper. It follows then, that maximum strengths from Cab-O-Sil® slips might be increased by firing at higher temperatures with some sacrifice in the time latitude available at 2200° F. Since considerable time latitude is available and its reduction could easily be tolerated, this approach deserves

investigation. Characterization at temperatures other than 2200° F might permit the estimation of activation energies for sintering and devitrification with sufficient accuracy to facilitate selection of an optimum sintering time-temperature.

The most difficult problem during this report period has been the pressing of Cab-O-Sil[®] for the production of mill feed. The large amount of labor required for this work has demanded that better methods be sought. Several alternate methods have been tried, but dry-pressing remains the most feasible with the equipment currently available. Consolidation of Cab-O-Sil[®] by isostatic pressing will be investigated during the next report period.

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SECTION IV

CONCLUSIONS

1. Filament wound structures of fused silica roving and an all fused silica binder are too dense for use as A-sandwich cores.
2. Incorporation of an organic tape with a fused silica binder and with or without fused silica filamentary material provides a porous structure suitable for A-sandwich core use but no stronger than conventional fused silica foams.
3. Porous structures with incorporated fused silica filaments were no stronger than foams having the same density.
4. Elastic modulus of high purity foamed silica was 1.5 times greater than that of conventional foamed silicas. Additional improvement is anticipated with sintering time-temperature changes.
5. The use of discontinuous fibers as reinforcement in foamed fused silica has thus far been unsuccessful due to devitrification and to particle to fiber bonding problems.
6. Fused silica honeycomb is easily prepared in flat sections by slip-casting techniques.
7. Slip-cast fused silica honeycomb structures are much stronger than random pore foamed fused silica of the same density.
8. Dry pressing and sintering of finely divided Cab-O-Sil[®] provides a consolidated material suitable for preparation of a fused silica casting slip by ball milling.

9. High purity fused silica bodies can be prepared by slip-casting and sintering at 2200° F to theoretical densities greater than 98 per cent and with elastic moduli more than twice that of bodies prepared from conventional fused silica slips.

SECTION V

RECOMMENDATIONS

Although the design goals of four times the strength of conventional foamed fused silica and twice the strength of dense fused silica skins were not reached during this contract year, considerable progress was made in improving the strength of both foamed and dense fused silica skins. Therefore, it is recommended that the milestone accomplishment chart continue to be followed as originally set down for the three year period with the following exceptions: (1) Fabrication and mechanical testing of "A" sandwich specimens to continue with the best presently available core materials (both honeycomb and foam) and dense skin materials, (2) Development work to produce better low-density, high-strength and high density, high-strength structures continue concurrently with the other phases. This concurrent continuation of materials development will not alter the scope or total cost of the contract. As better materials are developed they will be integrated into the fabrication and mechanical, electrical and thermal testing phases of the contract.

It is recommended that in continuing materials development the following items be specifically investigated.

1. Continue efforts to incorporate high modulus discontinuous fibers into high-purity foamed fused silicas. Emphasis to be placed on improving fiber-particulate bond.
2. Continue investigations on honeycomb structures and method of forming shapes other than flat plates.

3. Continue investigation of properties improvement of high purity fused silica foams by the parametric study currently in progress.
4. Improve methods for consolidation of Cab-O-Sil[®] into a compacted form in preparation for sintering to mill feed by such techniques as isostatic pressing and compaction on a metal rolling mill.
5. Investigate strength and casting characteristics of high purity slips using large experimental batches (3-5 gallons).
6. Investigate properties improvement of Cab-O-Sil[®] M-7 dense fused silica by time-temperature sintering studies above 2200° F.

APPENDIX

FILAMENT WINDING TERMINOLOGY

Circuit - One complete loop of the helical roving band on the mandrel. The starting and ending points of the loop lie in a plane normal to the longitudinal axis of the mandrel. The points do not necessarily coincide, but are indexed a fixed number of degrees on the perimeter of the cylindrical or rectangular portion of the mandrel. The circuit is the basic element of the winding geometry and is repeated during the course of winding to form other higher order systems.

Pattern - A number of repeated identical circuits. The first circuit of each pattern is contiguous to the first circuit of the previous pattern. The second circuit of each pattern is contiguous to the second circuit of the previous pattern, etc.

Layer - A multiplicity of circuits at the completion of which the mandrel is uniformly covered.

Helix Angle - The included acute angle formed by the intersection of the band on the body of the mandrel with a line on the body of the mandrel parallel to the longitudinal axis of the mandrel.

Winding Angle - Helix angle.

Mandrel - The core around which the filamentary material is wound.

Filament - A single fiber as drawn by the manufacturer. "Filament" is also used to designate a number of these fibers put together.

End - A number of filament grouped together. This number can vary but is not usually greater than 208.

Strand - A grouping of ends. The strand is the most common form of roving delivered from a serving package to a winding.

Roving - A broad classification of ends and/or strands in which the filaments are not twisted. Also used interchangeably with "strand" and "end."

Yarn - A group of twisted ends or strands.

Band - A term applied to the assemblage of rovings as they are wound on the mandrel.

Band width - The width of the band measured perpendicular to the direction of winding.

Size - A chemical surface treatment applied immediately after the fibers are formed. It provides both abrasion protection and coupling action with the matrix material.

Finish - A chemical coupling agent applied to a yarn or roving at some step before winding. It may replace the size or be in addition to the size.

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13. ABSTRACT Development of low and high density, high strength, amorphous silica for the construction of A-sandwich radomes is discussed. Techniques are described for forming low density, high strength structures by filament winding, slip-casting of honeycomb structures, and foaming of ultra-high purity amorphous silica. High density structures were slip-cast from a high purity slip formed by consolidation and subsequent ball milling of Cab-O-Sil [®] , a synthetic amorphous silica "fluff." The elastic modulus of the low density material was increased to 1.5 times that available from commercial fused silicas. Densities of 98 per cent of theoretical and elastic moduli of 9×10^{10} psi, approximately twice that attainable with commercial slip-cast fused silica, were achieved with the high density material. Firing times of 60 hours at 2200° F were possible without excessive cristobalite formation in the high purity silica as compared with 3 to 4 hours which was the maximum sintering time for commercial fused silicas without excessive devitrification.			

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